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On the Speed of Sublimation and Condensation

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It has been assumed that in the simplest case every atom that hits a crystal surface of the same material condenses. The corresponding speed of sublimation had been calculated theoretically. The formula for the equilibrium pressure is changed in the case of atoms, if the electron weight in the gaseous state is different from the solid state. The influence of this fact on the speed of sublimation is discussed in the first part of the paper and it is shown that for true metals the speed of sublimation is probably increased, while for non-metals a reflection coefficient exists. For molecules the equilibrium pressure is higher than for atoms because in sublimation there is a transition from a limited oscillation of the axes to free rotation. It is made plausible that this results in an increased speed of sublimation but a finite reflection coefficient might also occur.

STATISTICAL mechanics determines uniquely the vapor pressure or the equilibrium density of the saturated vapor over a crystal. On the other hand, equilibrium is present if the number of evaporating molecules is equal to that of the condensing. This relation is discussed in the following for several cases. It has a close connection with two recent papers that correlate the reaction velocity with the type of bond affected by the reaction.[1]

I. ATOMS

Given a crystal made up of atoms that have no resultant moment j; let Q_0 be the extrapolated heat of sublimation at zero temperature. Let furthermore ν be the (geometrical) average of the frequencies of vibration present in the crystal, then if the temperature is high enough to have classical specific heat $3R$, the number of vapor atoms per cc N_0 is given by[2]

$$N_0=(2\pi M/RT)^{\frac{1}{2}}\nu^3 \exp(-Q_0/RT)=K_0. \quad (1)$$

If the temperature is so low that the specific heat of the solid is zero,

$$N_0=(2\pi MRT)^{\frac{1}{2}}(Lh)^{-3} \exp(-Q_1/RT)=K_0' \quad (2)$$

(where L is the number of molecules per mole and Q_1 is Q_0 minus the zero point energy). In equilibrium the number of molecules condensing is[3]

$$(RT/2\pi M)^{\frac{1}{2}}N_0 \quad (3)$$

if one assumes that all atoms hitting the surface actually condense.[4] If we designate the number of atoms evaporating under this condition per second and cm² with k_0 and abbreviate

$$w=(RT/2\pi M)^{\frac{1}{2}}, \quad (3')$$

the x component of the average thermal velocity in the gas, there is in equilibrium:[5]

[1] O. K. Rice and H. Gershinowitz, J. Chem. Phys. **2**, 853 (1934); H. Eyring, J. Chem. Phys. **3**, 107 (1935).

[2] K. F. Herzfeld, *Kinetische Theorie der Wärme*, Braunschweig, 1925, p. 223.

[3] I. Langmuir, Phys. Rev. **8**, 149 (1916).

[4] This is in agreement with experiments on Hg, Cd, Zn by M. Knudsen, Ann. d. Physik **50**, 472 (1916); and R. W. Wood, Phil. Mag. **30**, 300 (1915); **32**, 364 (1916).

[5] The formula for k_0 which results from (4) has been deduced from kinetical considerations directly on p. 232 of book cited, footnote 2; see also R. Becker, Zeits. f. Physik **28**, 256 (1924).

$$k_0=wN_0 \quad \text{or} \quad k_0=wK_0, \tag{4}$$

or, at low temperatures

$$k_0'=wK_0'. \tag{4'}$$

Assume now we have an atom that has in the gaseous state a moment j, therefore an electron weight

$$g_v=2j+1,$$

while the crystal is not distinctly paramagnetic (this includes metals) so that the electron weight in the crystal is 1.

Then we have to replace (1), (2) by

$$N=K_0g_v \quad \text{or} \quad N=K_0'g_v. \tag{5}$$

If we call now the speed of evaporation k or k', we find

$$k=wN\alpha, \tag{6}$$

where $1-\alpha$ is the reflection coefficient, i.e., the fraction of the atoms that hit the surface but do not stick. Defining now a number β, $k=k_0\beta$, we find

$$\beta/\alpha=g_v. \tag{7}$$

The discussion is mainly concerned with (7).

(a) Emission of free electrons from a metal

Here $g_v=2$. The direct calculations of Nordheim[6] show that $\alpha=1$, $\beta=2$. The physical reason for this is that an electron entering the metal has such a high energy that it gets into an empty part of the energy band of the metal and can therefore enter, independent of the direction of its spin. On the other hand, there are, because of the spin, twice as many electrons of a given state in the metal than without spin, and therefore $\beta=2$.

(b) Metal with one valence electron in $S_{1/2}$

Here again $g_v=2$, because of the two possible spin orientations, while the experimental fact that there is no strong, temperature dependent paramagnetism shows that we need not consider different orientations in the crystal. Two cases must now be distinguished.

(b')

If the solid is a true metal and can therefore be considered according to Wigner, Seitz and Slater[7] as a lattice of positive ions surrounded by a sea of Fermi-electrons, one should expect $\alpha=1$. Each condensing atom would create two new neighboring states of opposite spin and therefore the electron of the condensing atom, in dissociating off, would find a ready free level. The ion, of course, having $j=0$, would always fit. This result is in agreement with Knudsen's experiments, who found that every atom of Ag and Cu condensed.[8] One must, however, account then for $\beta=2$ as a consequence.

The electron of a condensing atom will in general get into the free part of the energy band and drop down later. Therefore, from the principle of detailed balancing, one would expect that an ion ready to evaporate would in general pick up one of the few electrons in the unfilled part of the band. There will be accordingly certain electron states of energy Q_0'/L in which the electron "belongs" to a certain ion. The fraction of the ions that will have electrons in these states will be

$$2e^{-Q_0'/RT}, \tag{8}$$

the factor 2 coming from the two possible spin directions. The number of ions having such electrons that evaporate per second is then given by the formula (4) in which $Q_0''=Q_0-Q_0'$ is inserted, multiplied with (8), which gives $\beta=2$. If the one valence electron is in a state different from S in the vapor, while the conditions in the solid are as described here, the above considerations hold with

$$g_v=2j+1, \quad \beta=2j+1. \tag{b''}$$

If, on the other hand,[9] it were possible to condense these atoms into a monatomic, nonmetallic, diamagnetic crystal, in which, therefore, the atoms keep their valence electrons and have orientations of the moment fixed in the lattice, g_v would still be 2 (or $2j+1$ in general), g_s, the weight in the solid, 1. But now the considerations that led to the deduction of the evaporation

[6] L. Nordheim, Zeits. f. Physik **46**, 833 (1928); Proc. Roy. Soc. **A121**, 626 (1928).

[7] J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).

[8] M. Knudsen, Ann. d. Physik **50**, 472 (1916).

[9] A distinction analogous to that between (b') and (b'') is also made by J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932, p. 283, cases e, f.

formula (4) are valid without change, therefore $\beta=1$ and α must be $\frac{1}{2}$ (or $1/(2j+1)$ in general). This can easily be understood. If an atom comes down from the gas, only half (or in general the fraction $1/(2j+1)$) of the places on the crystal on which it can alight have as permitted direction of moment the one which the incoming atom has; this results in a reflection coefficient of the magnitude given above. Formally one can compare (b′) and (b″) so: A condensing atom with one valence electron creates two new states in the electron term-scheme of the crystal. But in the case (b′) the two levels corresponding to the two spin directions are very close together, in the case (b″) rather far (i.e., much farther than kT) apart.

(b‴)

If the crystal should be strongly paramagnetic, so that the j in both states would be the same and the components in the direction of a magnetic field the same, $g_v=g_s$, $\alpha=\beta=1$.

II. Molecules

We assume that the molecule in the crystal has, besides the vibrations of its center, rotatory oscillations of its axes (or axis for a linear molecule) around an equilibrium position.[10] We assume the temperature to be so high that these oscillations have their classical specific heat ($3R$, or $2R$ for a linear molecule), and that the specific heat of rotation in the gas has the classical specific heat ($(3/2)R$, or R for a linear molecule). Finally we assume that there is either no difference between the internal vibrations of the molecule in the gas and in the solid (the ν's remaining unchanged) or that in both states they do not contribute to the specific heat.

The vapor pressure formula is then

$$N=K_0K_r. \tag{9}$$

Here K_r is the ratio of the phase integrals of the rotational coordinates in the gaseous and the solid state. In classical calculations the phase integral can be split into a factor depending only on kinetic energy and momenta and one depending only on potential energy and coordinates. The former is independent of the forces and therefore the same for the gas and the crystal. Accordingly it drops out of K_r, which can then be written

$$K_r=\Phi_g\cdot\Phi_s^{-1}, \tag{10}$$

where Φ is only the integral over the coordinate space.

But we have always

$$\Phi_g\gg\Phi_s.$$

These quantities are, namely, the average steric angles covered by the motion and these are always much smaller for the crystal than for the unhampered rotation of the gas.

For example, for a diatomic molecule with unequal atoms (symmetry number 1), Φ_g is simply the full spherical angle 4π, while

$$\Phi_s=\int d\varphi\int \exp\left(-IL\omega^2\vartheta^2/2RT\right)\sin\vartheta d\vartheta, \tag{11}$$

where I is the moment of inertia, ω the average frequency of oscillation. This gives (putting ϑ for $\sin\vartheta$)

$$\Phi_s=2\pi RT/I\omega^2L,$$

or, e.g., with $\omega=3.10^{13}$, $I=10^{-39}$, $T=300$.

$$\Phi_s=4\pi\cdot 0.02$$

or $K_r\sim 50$.

We have then in general

$$\beta/\alpha=\Phi_g\Phi_s^{-1} \tag{12}$$

and again the question arises:

is $\beta=\Phi_g\Phi_s^{-1}$, i.e., very great, and $\alpha=1$ (13′)

or $\beta=1$, $\alpha=\Phi_s\Phi_g^{-1}$, i.e., very small (13″)

or does something between these extremes happen? Experimental results seem not available.

We are going to show that (13′) and (13″) follow clearly from two different assumptions. The assumption leading to (13′) seems more probable.

The question is the following. The heat of sublimation per mole, extrapolated to $T=0$, is Q_0. Consider a molecule in its heat motion. Assume that in a given moment it has a potential energy

[10] D. H. Andrews, Proc. Amst. Acad. **29**, 744 (1926); see also A. Eucken, Jahrb. f. Rad. **16**, 364 (1920); A. Eucken and E. Karwat, Zeits. f. physik. Chemie **112**, 479 (1924); A. Eucken and F. Fried, Zeits. f. Physik **32**, 151 (1925); F. Simon, ibid. **31**, 225 (1925).

(calculated from the equilibrium position) of ϵ, which is made of two parts, ϵ_t which is due to the deviations of the center of gravity of the molecule from its equilibrium position, and ϵ_r, which is due to a rotation of the axes out of the equilibrium orientation. If now the kinetic energy necessary to tear the molecule loose is given by

$$\epsilon' = Q_0/L - \epsilon = Q_0/L - \epsilon_t - \epsilon_r, \qquad (14')$$

that is, if the potential energy stored up by the oscillation of the axes is available for sublimation, (13′) holds. If, on the other hand, it is not available, that is, if the energy necessary to sublimate this molecule is

$$\epsilon' = Q_0/L - \epsilon_t \qquad (14'')$$

(13″) is true.

To prove that, start with the latter, simpler case. Then the deduction given for $k=k_0$ can be taken over without change, $\beta=1$. $\alpha=\Phi_s\Phi_g^{-1}$ can then be understood so that only such molecules can be condensed which come down under such an angle of the axes with the equilibrium position as it occurs at the temperature T in the crystal. (This is, of course, to be understood in the proper way, i.e., considering the distribution law.) The fraction of these properly oriented molecules is obviously given by the value of α mentioned above.

If, on the other hand, (14′) is true, we have to modify the deduction leading to (4) in the following manner:

Call q in general the coordinates that characterize the orientation of the axes, dq the corresponding element in the phase space. Then the fraction of the molecules that have deviations from the position of equilibrium between x and $x+dx\cdots$ and a direction of the axes between q and $q+dq$ is

$$\nu^3(2\pi M/RT)^{\frac{1}{2}} e^{-L\epsilon_t/RT} dxdydz \times \Phi_s^{-1} e^{-L\epsilon_r/RT} dq. \qquad (15)$$

The number of molecules hitting the surface (y, z plane) so that $m\dot{x}^2/2 \geqq Q_0/L - \epsilon$ is

$$n'(M/2\pi RT)^{\frac{1}{2}} \int_{(Q_0-L\epsilon)}^{\infty} \dot{x} \exp(-M\dot{x}^2/2RT) d\dot{x} = n'(RT/2\pi M)^{\frac{1}{2}} e^{-(Q_0-L\epsilon)/RT}, \qquad (16)$$

where n' is the number of the particular molecules per cc. Inserting (15) into (16) and integrating over $dxdydz$ and dq, one finds as number of evaporating molecules

$$\nu^3(2\pi M/RT)^{\frac{1}{2}} \exp -(Q_0/RT)(RT/2\pi M)^{\frac{1}{2}} \Phi_s^{-1} \int dq = k_0 \Phi_s^{-1} \int dq. \qquad (17)$$

But
$$\int dq = \Phi_g, \qquad (18)$$

and therefore
$$\beta = \Phi_g \Phi_s^{-1}.$$

In (18) it is understood, that the integration is to be taken according to classical physics, so that for example for a diatomic molecule with equal atoms, symmetry number 2,

$$\int dq = 2\pi = 4\pi/2.$$

In that case, $\alpha=1$. To understand why under these assumptions even badly oriented molecules condense, one has to reverse the reasoning used for (15′). The large forces involved in the large heat of condensation Q_0/L are sufficient to force the molecule into the lattice in whatever orientation it arrives, providing the necessary potential energy ϵ_r.

Under both assumptions (14′) and (14″), the kinetic energy of the oscillation of the axes is not involved in the process of sublimation. That means that each molecule keeps the angular momentum it had just before sublimation also in the gaseous state and each molecule keeps the angular momentum in the moment of condensation it had just before. Of course, angular momentum begins to change immediately after condensation, because of the forces now acting on the molecular orientation.

If the temperature rises so high that the molecules rotate almost freely in the crystal,

$$\Phi_g \sim \Phi_s, \quad \beta = \alpha = 1.$$

III. Refinement of the Theory

In the preceding deductions, one assumption has been made that might be wrong. The reasoning leading to (4) said: The number of atoms that have a deviation from the equilibrium position between x and $x+dx\cdots$ and evaporate per second is

$$n'(RT/2\pi M)^{\frac{1}{2}} \exp(-Q_0 + L\epsilon_t/RT), \qquad (19)$$

where ϵ_t is the potential energy connected with that deviation and n' the number of atoms per cc having this deviation. One then inserted n' from the Maxwell-Boltzmann distribution law and integrated over $dxdydz$. But that is correct only if in the permitted range $L\epsilon_t < Q_0$. Otherwise, one can only integrate to such values of x, y, z in (19) that

$$L\epsilon_t = Q_0.$$

Call $$\int_0^{L\epsilon_t=Q_0} dxdydz = 1/n''.$$

Then, in the simplest case, the number of evaporating atoms is

$$nk_0/n'' = \alpha' k_0,$$

where n is, as before, the number of atoms per cc, and speed of sublimation and speed of condensation have both to be multiplied by $\alpha' < 1$ in all the cases treated in I. The same is true for molecules and assumption (14''). Possibly Volmer's[11] experiments showing a reflection coefficient of Hg on mercury crystals of 10 percent can be explained so.

[11] M. Volmer and I. Estermann, Zeits. f. Physik **7**, 1 (1921).

Similarly for molecules, we have to change the discussion of assumption (14') so that we integrate only to such values of the coordinates in the crystal that satisfy

$$Q_0 > L(\epsilon_t + \epsilon_r).$$

The speed of sublimation $k_0\beta$ has again to be multiplied by a factor α' smaller than 1,

$$\alpha' = n\Phi_g^{-1} \int_0^{L\epsilon=Q_0} dxdydzdq = \Phi'\Phi_g^{-1}$$

and the same factor enters the formula for the speed of condensation, giving rise to a reflection coefficient of $1-\alpha'$.

The physical reason for the existence of this reflection coefficient is, of course, that the attractive forces that are responsible for the heat of sublimination can force the incoming molecule only into the fraction α' of the total coordinate space.

We have then an intermediate case between (13') and (13'') where

$$k = k_0\beta', \quad \beta' = \Phi'\Phi_s^{-1}, \quad \alpha' = \Phi'\Phi_g^{-1}.$$

I acknowledge gratefully the clarification of the problem due to discussions with Dr. M. Goeppert-Mayer.

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Non-Silicates with Cristobalite-Like Structure

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The cristobalite type of structure which has been previously observed in certain silicates: carnegieite, $NaAlSiO_4$, and Na_2CaSiO_4 is now shown to occur in $K_2O.Al_2O_3$, $K_2O.Fe_2O_3$, and $Na_2O.Al_2O_3$.

A NEW cubic compound, $K_2O.Al_2O_3$, has recently been described by Brownmiller,[1] and measurements on an x-ray powder photograph of it have been published.[2] This powder photograph is very similar to that of $K_2O.Fe_2O_3$, and they both resemble the x-ray patterns of certain silicates structurally isomorphous with cristobalite (see Table I). These similarities indicate that the structure of $K_2O.Al_2O_3$ and of $K_2O.Fe_2O_3$ may in some way or other be related to that of cristobalite.

The well-known feature of the cristobalite structure is the existence of endless silicon-oxygen chains with large, open spaces in between. It seemed probable, therefore, that in $K_2O.Al_2O_3$ there would be corresponding chains of alumi-

[1] L. T. Brownmiller, *A Study of the System Lime-Potash-Alumina*, Am. J. Sci. **29**, 260 (1935).

[2] The reflections observed by Brownmiller correspond to cubic symmetry (length of the edge of the unit cube, $a = 7.69$A), except for three weak lines, corresponding to a planar spacing of 2.395, 2.000 and 1.488. He states, however, that $K_2O.Al_2O_3$ is extremely hygroscopic so there were considerable difficulties in taking the photograph; it is probable, therefore, that these weak reflections come from some alteration product on the surface of the crystals.

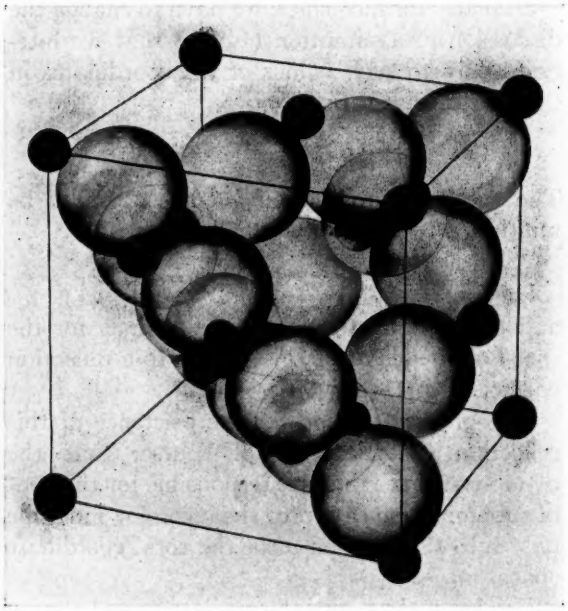

FIG. 1. The unit of the high-cristobalite structure. The large transparent balls represent oxygen ions, and the small black ones silicon ions, bringing out their relative size. The positions of the ions are very slightly displaced to give the structure a more regular arrangement than actually exists.

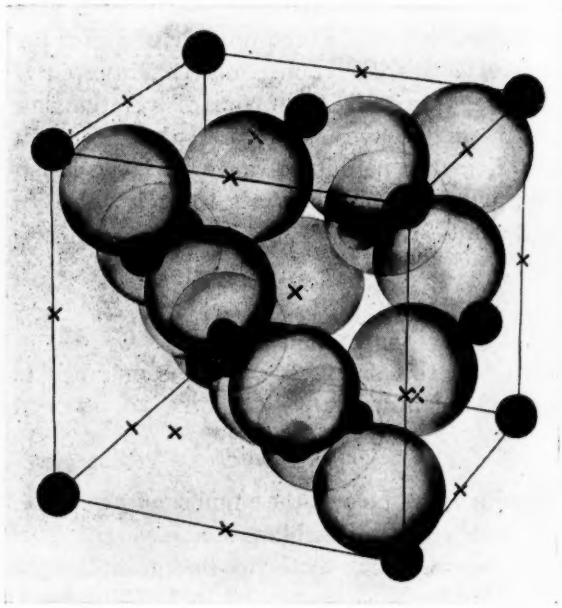

FIG. 2. The unit of the structure of $K_2Al_2O_4$ (and of $K_2Fe_2O_4$). The large transparent balls represent oxygen ions, and the small black ones aluminum ions, bringing out their relative size. In this way aluminum-oxygen chains are formed that are strictly analogous to the silicon-oxygen chains of cristobalite. The centers of the potassium atoms are indicated by crosses; the atoms themselves are so large as to fill up the interstices, touching 12 adjacent oxygens. The positions of the ions are very slightly displaced to give the structure a more regular arrangement than actually exists.

num-oxygen, and in $K_2O.Fe_2O_3$ chains of iron-oxygen, with the potassium atoms situated in the interstices.[3]

TABLE I. *Intensity of powder diffraction lines of α-carnegieite, Na_2CaSiO_4, $K_2Fe_2O_4$ and of $K_2Al_2O_4$.*

	Carnegieite	Na_2CaSiO_4	$K_2Fe_2O_4$		$K_2Al_2O_4$	
Indices	Obs.	Obs.	Obs.	Calc.	Obs.*	Calc.
111	10	3	4	2.2	0	0.2
022	9	10	10+	15.1	*ss*	15.0
113	0.5	0.5	0	0.1	*m*	3.5
222	3	1	1	0.9	*w*	1.7
004	1	4	4	1.8	*m*	1.2
133	4	0.5	1	1.0	0	0.1
224	6	6	8	10.0	*s*	10.0
333, 115	2	1	1	0.3	0	0.6
044	3	3	3	5.5	*m*	6.3
135	2	1	1	0.8	0	0.0
026	2	2	5	5.0	*s*	5.4
335	0	0.5	0	0	0	0
444	0.5	0.5	0.5	0.8	*w*	0.7
117, 155	0	0.5	0	0	0	0
246	1	1	2	6.5	*m*	6.5
355, 137	0.5	—	—	0	0	0
066, 228	—	—	—	3.4	*w*	3.1
048	—	—	—	1.4	*w*	1.0
466	—	—	—	—	*w*	1.4
a_0	7.37	7.48	7.99		7.69	

* Observed intensities as given by Brownmiller.

[3] For a description of the cristobalite structure, and of the structure of carnegieite and Na_2CaSiO_4, which have the same type of structure, see Barth and Posnjak, *Silicate Structures of the Cristobalite Type: III, Structural Relationship of High-Cristobalite, α-Carnegieite, and Na_2CaSiO_4*, Zeits. f. Krist. **81**, 376 (1932).

The constituent atoms in cristobalite (and in the silicates isomorphous with it) show a close approach to a face-centered arrangement with silicons close to 4*b*, 4*d*; and oxygens close to 16*a*.[4] In $K_2O.Al_2O_3$ one would expect, therefore, Al to be in 4*b*, 4*d*; and the oxygens to be in 16*a*, or very nearly in these positions. The only possible place for the K-atoms would then be 4*c*, 4*e*. The same holds, of course, for $K_2O.Fe_2O_3$ with interchange of Fe and Al.

We can test this assumption by calculating the intensities which, if this represents the true structure of $K_2O.Al_2O_3$ and $K_2O.Fe_2O_3$, must be proportional to the observed ones.

Table I shows that there is a fair agreement between calculated and observed intensities, and it can be concluded, therefore, that the structure

[4] Wyckoff's notation.

of $K_2O.Al_2O_3$ and of $K_2O.Fe_2O_3$ is of the cristobalite type.

A few years ago it was shown that the structure of cristobalite was not exactly face-centered but actually built upon a simple lattice.[5] Also certain silicates isomorphous with cristobalite exhibit the same small, but characteristic deviation from a face-centered lattice.[6]

An inspection of Table I shows that $K_2O.Al_2O_3$ and $K_2O.Fe_2O_3$ also seem to deviate slightly from the face-centered arrangement. The discrepancies between observed and calculated intensities are small, but significant; thus 400 is always stronger than demanded by the theory, which is again exactly the same phenomenon previously observed in cristobalite and its congeners. This means that the structural arrangement we have been considering so far is not accurate, it represents only the approximate or idealized structure, whereas the true structure is slightly different and actually isomorphous with the space group T^4. (The arguments for T^4 are exactly the same as in the case of cristobalite.)

From this it follows that the true structure of $K_2O.Al_2O_3$ is conditioned by no less than 8 independent parameter values: 4K+4K, 4Al+4Al, and $4O_I$ in position 4*f*, each group of four with one parameter, and the remaining $12O_{II}$ in the general positions of T^4 with three parameters. These 8 parameters cannot be determined accurately from powder photographs. But in the case of $K_2O.Fe_2O_3$ a trial calculation has been made which shows that the discrepancies between calculated and observed intensities are appreciably diminished by moving the oxygen atoms slightly out of the idealized positions, following thereby exactly the same procedure previously described in the case of carnegieite and Na_2CaSiO_4.

Figs. 1 and 2 show very plainly the relation between the structure of cristobalite and the structure of $K_2O.Al_2O_3$ (or $K_2O.Fe_2O_3$). Al (and Fe) has coordination number 4, K has 12.

The interatomic distances in the idealized structures are as follows:

For $K_2O.Al_2O_3$: O $-$O$=2.72$A,
Al $-$O$=1.66$A,
K $-$O$=3.19$A;
For $K_2O.Fe_2O_3$: O $-$O$=2.82$A,
Fe$-$O$=1.73$A,
K $-$O$=3.32$A.

It is noteworthy that the distances Al$-$O and Fe$-$O are smaller than usual even for coordination number 4,[7] a phenomenon which also has its strict analogy in the silicate structures of the cristobalite type.

As has long been known, mixed crystals of α-carnegieite and cristobalite exist.[8] But it has now been observed that α-carnegieite is able to take up also $Na_2O.Al_2O_3$ in solid solution; indeed, it is possible that a continuous series of solid solutions extends all the way between carnegieite and $Na_2O.Al_2O_3$.[9] Consequently $Na_2O.Al_2O_3$ must be isomorphous with carnegieite and the structure type of at least one of its modifications (potential or real) must therefore be that of $K_2O.Al_2O_3$. This becomes so much the more probable since powder photographs of $Na_2O.Al_2O_3$ at ordinary temperature exhibit an interesting similarity to those of low-carnegieite. To be sure, the low-carnegieite pattern merges gradually into that of low-$Na_2O.Al_2O_3$ through intermediate mix-crystals with successively decreasing amounts of silica.[10]

Thus we see that the cristobalite type of structure is not restricted to silicates only, but that at least two aluminates and one ferrite crystallize in the same structure.

Note added in proof: In a paper by S. Hilpert and A. Lindner measurements of x-ray powder photographs of $K_2O.Fe_2O_3$, $Rb_2O.Fe_2O_3$, and $PbO.Fe_2O_3$ have been published (Zeits. f. physik. Chemie **B22**, 400 (1933)). From these measurements it can be deduced that $Rb_2O.Fe_2O_3$ and $PbO.Fe_2O_3$ are isomorphous with $K_2O.Fe_2O_3$, and consequently that these two additional ferrites also crystallize in the cristobalite type of structure.

[5] T. F. W. Barth, Am. J. Sci. **23**, 350 (1932).
[6] T. F. W. Barth and E. Posnjak, Zeits. f. Krist. **81**, 135, 371 (1932).
[7] For discussion and values of interatomic distances in relation to coordination number see W. H. Zachariasen, Zeits. f. Krist. **80**, 137 (1931).
[8] Cf. Barth and Posnjak, *Silicate Structures of the Cristobalite Type: III*, Zeits. f. Krist. **81**, 385 (1932).
[9] Unpublished experiments by J. F. Schairer of this Laboratory.
[10] These mixtures were prepared by Dr. J. F. Schairer.

The Moles of Vibration of Butane and Pentane. "Free Rotation" about Carbon-Carbon Bonds and a New Type of Stereoisomerism[1]

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The Hamiltonian function for a chain of four carbon atoms with the simple valence force system potential energy is transformed by successive changes of variables to such a form that the wave equation is nearly separable into five harmonic oscillator equations and a sixth equation governing the internal rotation. This rotation equation has been solved numerically for twelve different rotational levels of the nonvibrating molecule, some of which actually correspond to rotations, others to a torsional oscillation of restricted amplitude about either the *cis* or the *trans* position. The remaining terms in the wave equation are treated as a perturbation; the first-order perturbation energy is less than 1 cm^{-1} for all moderately low vibrational states. There are thus two isomeric forms of butane with plane carbon skeletons, and a third form in which the two ethyl groups are rotating about the central carbon-carbon bond. The vibration frequencies for the three possible plane forms of a five-carbon chain have been calculated. When the frequencies of C_2, C_3, C_4 and C_5 are calculated with the same two force constants throughout, and by taking account of the two plane forms of C_4 and the three of C_5, results are obtained in fair statistical agreement with observed Raman and infrared lines.

INTRODUCTION

VERY little work has been done on the motions of molecules which are capable of internal rotations. Nielsen[3] has studied a generalization of the symmetrical top, one with an extra degree of torsional freedom about the symmetry axis, and LaCoste[4] has treated the spherical top with four symmetric tetrahedrally arranged gyroscopes. These investigations of models of ethane and tetramethylmethane, respectively, both deal with the interaction between external and internal rotation for nonvibrating molecules. The present paper is an attempt to consider the interaction of the internal rotation with vibration. This interaction will be relatively small for the foregoing molecules; for saturated hydrocarbons with a chain of four or more carbon atoms, the internal rotation changes the shape of the carbon skeleton, and a relatively large interaction results. Because of the considerable difference in mass between carbon and hydrogen atoms, there is little interaction between C−H and C−C vibrations, and useful results probably can be obtained by treating the carbon skeleton alone. In addition to neglect of the hydrogen atoms, and treatment only of states in which the total angular momentum of the molecule is zero, it is necessary to use the simplest possible valence-force potential function

$$V=(k/2)\sum_i \overline{\Delta d_i}^2+(b/2)\sum_j d^2\overline{\Delta\theta_j}^2, \qquad (1)$$

where d_i and θ_j are the bond lengths and bond angles; d, the equilibrium bond length, has been introduced in the second term to make k and b dimensionally homogeneous. With these three simplifications, it becomes possible to give a fairly complete solution of the problem.

For completeness, we give the results for C_2 and C_3 based on the foregoing assumptions. In terms of λ defined by

$$\nu=(1/2\pi)\lambda^{1/2} \qquad (2)$$

they are

$$C_2:\ \lambda=2k/m, \qquad (3)$$

$$C_3:\ \lambda=(7/3)(k/m), \qquad (4)$$

$$\lambda=(5/3)(k/m)+(16/15)(b/m)+(288/125)(b^2/km)+\cdots, \qquad (5)$$

$$\lambda=(18/5)(b/m)-(288/125)(b^2/km)+\cdots, \qquad (6)$$

the last two values being roots of

$$\lambda^2-(5k+14b)(\lambda/3m)+6bk/m^2=0. \qquad (7)$$

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[3] Nielsen, Phys. Rev. **40**, 445 (1932).

[4] LaCoste, Phys. Rev. **46**, 718 (1934).

Hamiltonian for the C_4 Chain

The coordinates in which the potential energy is written are shown in Fig. 1. It is desirable to make the substitutions

$$d_1+d_3=d\epsilon_1, \quad d_2=d\epsilon_2, \quad d_1-d_3=d\epsilon_3, \tag{8}$$

$$\theta_1+\theta_2=\eta_1, \quad \theta_1-\theta_2=\eta_2. \tag{9}$$

The kinetic energy is most easily obtained from auxiliary Cartesian coordinates referred to the center of gravity as origin, thus excluding translational energy. It is not feasible to exclude rotational energy of the whole molecule as can be done in simpler problems by using an auxiliary system which rotates with the molecule. The method used here should be generally useful for polyatomic molecules of low symmetry. We first calculate the kinetic energy of vibration plus rotation

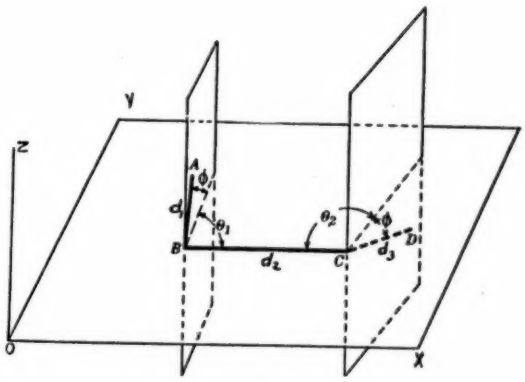

Fig. 1.

$$T'=(m/2)\sum_{i=1}^{4}(\dot{x}_i^2+\dot{y}_i^2+\dot{z}_i^2)=(md^2/2)[(9-4\gamma^2)\dot{\epsilon}_1^2/18+\dot{\epsilon}_1\epsilon_2/3+2^{1/2}\gamma^2\dot{\epsilon}_1\dot{\eta}_1/9+8\gamma\delta\dot{\epsilon}_1\dot{\varphi}/9+\dot{\epsilon}_2^2$$
$$+2^{3/2}\dot{\epsilon}_2\dot{\eta}_1+(6-\gamma^2)\dot{\eta}_1^2/12-2^{3/2}\gamma\delta\dot{\eta}_1\dot{\varphi}/9+8(1-\gamma^2)\dot{\varphi}^2/9]$$
$$+(md^2/2)[(9+8\gamma^2)\dot{\epsilon}_3^2/36-2^{1/2}\gamma^2\epsilon_3\dot{\eta}_2/9+(4+\gamma^2)\dot{\eta}_2^2/36], \tag{10}$$

where

$$\gamma=\cos\varphi, \quad \delta=\sin\varphi. \tag{11}$$

This expression is not exact, having been obtained by putting $d_1=d_2=d_3=d$ and $\theta_1=\theta_2=\cos^{-1}(-1/3)$ wherever functions of these variables occur as coefficients in $\dot{x}_i$, $\dot{y}_i$ and $\dot{z}_i$, in accordance with the usual custom in treating small vibrations. No similar substitution is possible for φ, and as a result the quadratic form for T' does not have constant coefficients. The error introduced at this stage could be reduced by the perturbation-theory methods recently used by Bonner[5] for the water molecule, but this refinement would be wasted in the present crude treatment.

The next step is to determine the external rotational energy of the whole molecule, which must be subtracted from (10). The moments of inertia are

$$A=m\sum(y_i^2+z_i^2)=(md^2/9)(16-8\gamma^2); \quad B=m\sum(x_i^2+z_i^2)=(md^2/9)(33-16\gamma^2);$$
$$C=m\sum(x_i^2+y_i^2)=(md^2/9)(17+8\gamma^2) \tag{12}$$

and there is one nonvanishing product of inertia

$$E=(10/9)2^{1/2}md^2\delta. \tag{13}$$

The angular momenta about the Cartesian axes are

$$M_x=(md^2/9)[4\gamma\delta\epsilon_3-2^{1/2}\gamma\delta\dot{\eta}_2], \quad M_y=(md^2/9)[3\cdot2^{1/2}\delta(\dot{\epsilon}_1-2\dot{\epsilon}_2)-(21/2)\delta\dot{\eta}_1+5\cdot2^{1/2}\gamma\dot{\varphi}],$$
$$M_z=(md^2/9)[-4\cdot2^{1/2}\gamma\dot{\epsilon}_3+(13/2)\gamma\dot{\eta}_2]. \tag{14}$$

It is shown in the Appendix that the rotational energy is

$$T_{\text{rot}}=\tfrac{1}{2}[M_y^2/B+(CM_x^2+2EM_xM_z+AM_z^2)/(AC-E^2)]. \tag{15}$$

When this rotational energy is subtracted, the kinetic energy of vibration is found to be

[5] Bonner, Phys. Rev. **46**, 458 (1934).

$$T=[md^2/(297-144\gamma^2)][(261/4-60\gamma^2+16\gamma^4)\dot{\epsilon}_1^2+(171/2-60\gamma^2)\dot{\epsilon}_1\dot{\epsilon}_2+2^{1/2}(63/2-15\gamma^2-8\gamma^4)\dot{\epsilon}_1\dot{\eta}_1$$
$$+\gamma\delta(72-64\gamma^2)\dot{\epsilon}_1\dot{\varphi}+(225/2-36\gamma^2)\dot{\epsilon}_2^2+2^{1/2}(36+15\gamma^2)\dot{\epsilon}_2\dot{\eta}_1+120\gamma\delta\dot{\epsilon}_2\dot{\varphi}+(153/8+15\gamma^2+2\gamma^4)\dot{\eta}_1^2$$
$$+2^{1/2}\gamma\delta(72+16\gamma^2)\dot{\eta}_1\dot{\varphi}+(132-32\gamma^2-64\gamma^4)\dot{\varphi}^2]+[m/(72+192\gamma^2-64\gamma^4)][(9+24\gamma^2)\dot{\epsilon}_3^2$$
$$+12\cdot 2^{1/2}\gamma^2\dot{\epsilon}_3\dot{\eta}_2+9\dot{\eta}_2^2]. \quad (16)$$

The potential energy in these coordinates is

$$V=[(k\overline{\Delta\epsilon_1}^2/4+k\overline{\Delta\epsilon_2}^2/2+b\overline{\Delta\eta_1}^2/4)+(k\overline{\Delta\epsilon_3}^2/4+b\overline{\Delta\eta_2}^2/4)]d^2. \quad (17)$$

If γ were not a function of φ, one would now find by straightforward calculation in the usual way that the frequencies were $(1/2\pi)\lambda^{1/2}$ where the λ were roots of

$$\lambda^2-[2k+(2/3)(3+8\gamma^2)b](\lambda/m)+(4/9)(9+24\gamma^2-8\gamma^4)(bk/m^2)=0 \quad (18)$$

and

$$\lambda^4-[4k+(22-16\gamma^2)b/3]\lambda^3/m+[34k^2/9+(8/9)(27-16\gamma^2-4\gamma^4)bk]\lambda^2/m^2$$
$$-(4/9)(33-8\gamma^2-16\gamma^4)bk^2\lambda/m^3=0. \quad (19)$$

These roots may be expressed conveniently as power series in b/k, which is about 0.1; they then become

$$\lambda_1=2k/m+(16/9)\gamma^4b/m+(16/9)\gamma^4[1+(8/3)\gamma^2-(8/9)\gamma^4]b^2/km+\cdots,$$
$$\lambda_2=2[1+(8/3)\gamma^2-(8/9)\gamma^4]b/m-(16/9)\gamma^4[1+(8/3)\gamma^2-(8/9)\gamma^4]b^2/km+\cdots \quad (20)$$

and

$$\lambda_3=(2+2^{1/2}/3)k/m+(4/51)[(22-28\gamma^2+12\gamma^4)-2^{1/2}(15-16\gamma^2+2\gamma^4)]b/m+\cdots,$$
$$\lambda_4=(2-2^{1/2}/3)k/m+(4/51)[(22-28\gamma^2+12\gamma^4)+2^{1/2}(15-16\gamma^2+2\gamma^4)]b/m+\cdots,$$
$$\lambda_5=(2/17)(33-8\gamma^2-16\gamma^4)b/m-(16/4913)(33-8\gamma^2-16\gamma^4)(81-100\gamma^2+38\gamma^4)b^2/km+\cdots, \quad (21)$$
$$\lambda_6=0.$$

The linear transformation which would reduce (16) and (17) to

$$T=(md^2/2)\left\{\sum_{i=1}^{5}\dot{u}_i^2+\frac{8}{9}\frac{33-8\gamma^2-16\gamma^4}{33-16\gamma^2}\dot{u}_6^2\right\}, \quad (22)$$

$$V=(md^2/2)\sum_{i=1}^{5}\lambda_iu_i^2 \quad (23)$$

is

$$\Delta\epsilon_3=-2u_1+(4/9)2^{1/2}\gamma^2(9+24\gamma^2-8\gamma^4)^{1/2}(b/k)u_2, \quad (24a)$$
$$\Delta\eta_2=(4/3)2^{1/2}\gamma^2u_1+(2/3)(9+24\gamma^2-8\gamma^4)^{1/2}u_2, \quad (24b)$$
$$\Delta\epsilon_1=(2+2^{1/2}/3)^{1/2}u_3+(2-2^{1/2}/3)^{1/2}u_4+(4/17)(7-6\gamma^2)[(2/17)(33-8\gamma^2-16\gamma^4)]^{1/2}(b/k)u_5, \quad (24c)$$
$$\Delta\epsilon_2=(1+2^{1/2}/6)^{1/2}u_3+(1-2^{1/2}/6)^{1/2}u_4+(4/17)(4-\gamma^2)[(2/17)(33-8\gamma^2-16\gamma^4)]^{1/2}(b/k)u_5, \quad (24d)$$
$$\Delta\eta_1=[(4-2^{5/2})+2^{5/2}\gamma^2][(1/17)(1-2^{1/2}/6)]^{1/2}u_3$$
$$+[-(4+2^{5/2})+2^{5/2}\gamma^2][(1/17)(1+2^{1/2}/6)]^{1/2}u_4+[(4/17)(33-8\gamma^2-16\gamma^4)]^{1/2}u_5, \quad (24e)$$
$$\varphi=\gamma\delta[(1/17)(1-2^{1/2}/6)]^{1/2}u_3+\gamma\delta[(1/17)(1+2^{1/2}/6)]^{1/2}u_4$$
$$+2\gamma\delta(9+2\gamma^2)[(17/2)(33-8\gamma^2-16\gamma^4)]^{-1/2}u_5+u_6, \quad (24f)$$

where every coefficient is merely the leading term of a power series in b/k. The substitution (24) does still lead to (22) and (23), even though γ is a function of the old variable φ, but of course the old variables have not been completely eliminated. We note, however, that u_6 is the only one of the new variables which is not associated with a small amplitude vibration. We can therefore express γ explicitly by means of power series in the u_i

$$\gamma=\cos u_6\Big[1+\sum_{i,\,j=3}^{5} a_{ij}u_iu_j+\cdots\Big]+\sin u_6\Big[\sum_{i=3}^{5} b_iu_i+\cdots\Big]. \tag{25}$$

The coefficients a_{ij}, b_i, etc., could be evaluated by substitution of (25) into (24); when (25) is substituted into (22) and (23), however, one sees that the b_i occur only in terms of at least the third degree, and the a_{ij} in terms of at least the fourth degree. Since third-degree terms have been neglected from the beginning in both T and V, we continue to neglect them here and adopt the new definition

$$\gamma=\cos u_6. \tag{26}$$

In terms of the momenta, (22) becomes

$$T=(1/2md^2)\Big[\sum_{i=1}^{5} p_i^2+\frac{9}{8}\frac{33-16\gamma^2}{33-8\gamma^2-16\gamma^4}p_6^2\Big]. \tag{27}$$

We have now obtained the Hamiltonian in a form for which the variables are nearly separated.

Wave-Mechanical Treatment of the C_4 Chain

Writing the wave equation by the method of Condon and Morse[6] and making the substitutions

$$u_i=(h/2\pi)^{1/2}(mkd^4)^{-1/2}v_i,\quad i=1,\,2,\,3,\,4,\,5;\quad u_6=v_6,\quad (1/2\pi)(k/m)^{1/2}=\nu_0,\quad \lambda_i=(k/m)\rho_i \tag{28}$$

we obtain

$$\sum_{i=1}^{5}\frac{\partial^2\psi}{\partial v_i^2}+A\frac{\partial^2\psi}{\partial v_6^2}+B\frac{\partial\psi}{\partial v_6}+\Big(\frac{2W}{h\nu_0}-\sum_{i=1}^{5}\rho_iv_i^2\Big)\psi=0, \tag{29}$$

where

$$\begin{aligned}A&=(9h/32\pi^2md^2\nu_0)(33-16\gamma^2)/(33-8\gamma^2-16\gamma^4),\\ B&=(27h/4\pi^2md^2\nu_0)\gamma\delta(33-132\gamma^2+32\gamma^4)/(33-8\gamma^2-16\gamma^4)^2.\end{aligned} \tag{30}$$

We shall solve this equation by a perturbation method. Let

$$\partial^2\psi_i/\partial v_i^2+(2W_i/h\nu_0-\rho_iv_i^2)\psi_i=0,\qquad i=1,\,2,\,3,\,4,\,5, \tag{31}$$

$$A\partial^2\psi_6/\partial v_6^2+B\partial\psi_6/\partial v_6+(2/h\nu_0)(W_6-\sum_{i=1}^{5}W_i)\psi_6=0. \tag{32}$$

Since the ρ_i in (31) are functions of γ and therefore of v_6, the W_i are also functions of v_6, and thus play the role of a potential energy in (32). It is then easily seen that

$$\psi_0=\psi_1\psi_2\psi_3\psi_4\psi_5\psi_6 \tag{33}$$

satisfies

$$\sum_{i=1}^{5}\frac{\partial^2\psi_0}{\partial v_i^2}+A\frac{\partial^2\psi_0}{\partial v_6^2}+B\frac{\partial\psi_0}{\partial v_6}+\Big[\frac{2W_6}{h\nu_0}-\sum_{i=1}^{5}\rho_iv_i^2+V^1\Big]\psi_0=0, \tag{34}$$

where

$$-V^1=A\sum_{i=1}^{5}\frac{1}{\psi_i}\frac{\partial^2\psi_i}{\partial v_6^2}+2A\frac{1}{\psi_6}\frac{\partial\psi_6}{\partial v_6}\sum_{i=1}^{5}\frac{1}{\psi_i}\frac{\partial\psi_i}{\partial v_6}+2A\sum_{i=j+1}^{5}\sum_{j=1}^{4}\frac{1}{\psi_i}\frac{\partial\psi_i}{\partial v_6}\frac{1}{\psi_j}\frac{\partial\psi_j}{\partial v_6}+B\sum_{i=1}^{5}\frac{1}{\psi_i}\frac{\partial\psi_i}{\partial v_6}. \tag{35}$$

[6] Condon and Morse, *Quantum Mechanics*, McGraw-Hill, 1929, p. 15.

Then if ψ_0 is taken as the zeroth-order solution of (29), the perturbation potential is evidently V^1, and the first-order perturbation energy is

$$2W^1/h\nu_0=\int_{v_6}\int_{v_5}\int_{v_4}\int_{v_3}\int_{v_2}\int_{v_1}\psi_0^2V^1d\tau. \tag{36}$$

Now since

$$\int_{-\infty}^{\infty}\psi_i^2dv_i=1 \tag{37}$$

we find by differentiation with respect to v_6

$$\int_{-\infty}^{\infty}\psi_i\frac{\partial^2\psi_i}{\partial v_6^2}dv_i=-\left(\frac{d\rho_i}{dv_6}\right)^2\int_{-\infty}^{\infty}\left(\frac{\partial\psi_i}{\partial\rho_i}\right)^2dv_i=-\frac{n_i^2+n_i+1}{32\rho_i^2}\left(\frac{d\rho_i}{dv_6}\right)^2 \quad (i=1, 2, 3, 4, 5), \tag{38}$$

where the last result makes use of the fact that the ψ_i are normalized solutions of (31) and therefore are

$$\psi_i=\rho_i^{1/8}\pi^{-1/4}(2^{n_i}n_i!)^{-1/2}\exp(-2^{-1}\rho_i^{1/2}v_i^2)H_{n_i}(\rho_i^{1/4}v_i) \qquad (i=1\cdots5) \tag{39}$$

and uses also various well-known properties of the Hermitian polynomials. Most of the terms in (36) vanish and the first-order perturbation energy reduces to

$$\frac{2W^1}{h\nu_0}=-\int_0^{2\pi}\frac{A\psi_6^2}{32}\sum_{i=1}^{5}(n_i^2+n_i+1)\rho_i^{-2}\left(\frac{d\rho_i}{dv_6}\right)^2dv_6. \tag{40}$$

The zeroth-order energy, of course, is

$$2W^0/h\nu_0=2W_6/h\nu_0. \tag{41}$$

This is as far as the analytic solution can be carried; (32) is not amenable to anything except numerical solution. Fig. 2 and Table I show the dependence of the $\rho_i^{1/2}$ upon φ, calculated numerically from (18) and (19) for the case $b/k=0.1$, and also the composite $(1/2)\sum_{i=1}^{5}\rho_i^{1/2}$, which is the potential energy term for (32) when all five vibrational quantum numbers are zero. This curve has a period of π, and is symmetric about $\varphi=0,\ \pi/2,\ \pi\cdots$. The differential terms in (32) likewise are seen to be symmetric about $\varphi=0,\ \pi/2,\ \pi\cdots$. The internal configuration of the atoms has a period of π, but a change of 2π is required to bring the molecule back to its original position. We therefore require solutions of (32) subject to the boundary condition

$$\psi_6(\varphi)=\psi_6(\varphi+2\pi). \tag{42}$$

TABLE I. *Values of $\rho_i^{1/2}$ for C_4 with $b/k=0.1$.*

φ	$\rho_1^{1/2}$	$\rho_2^{1/2}$	$\rho_3^{1/2}$	$\rho_4^{1/2}$	$\rho_5^{1/2}$	$(1/2)\Sigma$
0°	1.49550	0.70484	1.58475	1.26027	0.31667	2.68101
15°	1.48503	.70165	1.58275	1.26572	.35853	2.69684
30°	1.45968	.68508	1.57800	1.28387	.44148	2.72405
45°	1.43385	.64864	1.57347	1.31594	.50908	2.74049
60°	1.41888	.56578	1.57215	1.35435	.54231	2.72673
75°	1.41453	.48458	1.57433	1.38417	.55061	2.70411
90°	1.41421	.44721	1.57607	1.39496	.55084	2.69164

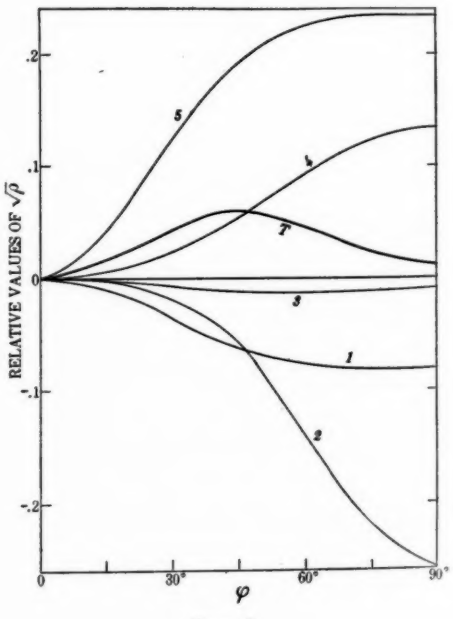

FIG. 2.

TABLE II. *Rotational eigenfunctions.*

ψ_6

φ	V, cm^{-1}	0_{SS}	2_{SA}	2_{AS}	4_{SS}	4_{AA}	6_{SA}	6_{AS}	8_{AA}	8_{SS}	12_{AA}	16_{AA}	20_{AA}
0°	0.000	2.330213	2.330308	0.00000	−0.03222	0.00000	−0.12917	0.00000	0.0000	−0.634	0.000	0.000	0.000
3°	.377	2.303053	2.303147	.00217	−.03171	.22343	−.12548	.42040	.3677	−.610	.295	.481	.584
6°	1.486	2.222462	2.222551	.00431	−.03013	.43731	−.11357	.82077	.7179	−.532	.567	.893	1.042
9°	3.283	2.091441	2.091524	.00642	−.02749	.63155	−.09364	1.18004	1.0327	−.403	.787	1.175	1.277
12°	5.688	1.915922	1.915995	.00850	−.02387	.79615	−.06654	1.48082	1.2937	−.230	.931	1.277	1.220
15°	8.601	1.705351	1.705412	.01054	−.01943	.92225	−.03314	1.70481	1.4848	−.024	.977	1.170	.861
18°	11.891	1.472545	1.472592	.01259	−.01426	1.00383	.00495	1.84017	1.5948	.202	.914	.856	.267
21°	15.425	1.232386	1.232418	.01476	−.00854	1.03933	.04608	1.88352	1.6200	.428	.741	.378	−.428
24°	19.048	0.999585	0.999601	.01721	−.00235	1.03255	.08872	1.84184	1.5660	.641	.473	−.190	−1.047
27°	22.614	.786517	.786514	.02024	.00431	.99219	.13194	1.72956	1.4466	.827	.137	−.753	−1.420
30°	25.974	.601576	.601554	.02427	.01160	.93014	.17589	1.56996	1.2802	.980	−.233	−1.215	−1.436
33°	28.991	.448620	.448574	.02983	.02012	.85940	.22170	1.38437	1.0864	1.098	−.605	−1.504	−1.079
36°	31.548	.327469	.327392	.03782	.03050	.79209	.27177	1.19324	.8820	1.188	−.948	−1.579	−.442
39°	33.543	.235073	.234957	.04936	.04394	.73830	.32951	1.01202	.6789	1.256	−1.243	−1.434	.319
42°	34.903	.166842	.166666	.06609	.06213	.70564	.39930	.84933	.4834	1.312	−1.470	−1.097	1.010
45°	35.579	.117781	.117523	.09024	.08735	.69949	.48596	.71274	.2963	1.362	−1.626	−.621	1.457
48°	35.555	.083247	.082872	.12483	.12273	.72331	.59443	.59960	.1151	1.410	−1.705	−.068	1.549
51°	34.840	.059342	.058798	.17376	.17224	.77900	.72904	.50738	−.0650	1.556	−1.700	.487	1.268
54°	33.478	.043014	.042230	.24187	.24076	.86661	.89248	.43204	−.2486	1.493	−1.592	.971	.686
57°	31.535	.031998	.030873	.33473	.33391	.98363	1.08419	.36844	−.4388	1.510	−1.400	1.314	−.049
60°	29.106	.024675	.023077	.45810	.45751	1.12385	1.29854	.31156	−.6348	1.493	−1.097	1.456	−.754
63°	26.303	.019918	.017682	.61702	.61659	1.27606	1.52299	.25682	−.8307	1.422	−.700	1.363	−1.245
66°	23.256	.016950	.013881	.81441	.81412	1.42317	1.73694	.20031	−1.0143	1.281	−.235	1.034	−1.390
69°	20.109	.015239	.011118	1.04940	1.04923	1.54234	1.91180	.13996	−1.1675	1.057	.254	.513	−1.144
72°	17.000	.014406	.009005	1.31572	1.31565	1.60686	2.01348	.07508	−1.2668	.748	.706	−.108	−.569
75°	14.079	.014168	.007276	1.60060	1.60062	1.58998	2.00755	.00711	−1.2894	.369	1.054	−.700	.175
78°	11.479	.014300	.005749	1.88487	1.88497	1.47023	1.86630	−.06041	−1.2158	−.048	1.232	−1.127	.864
81°	9.320	.014618	.004306	2.14455	2.14471	1.23733	1.57647	−.12219	−1.0369	−.456	1.199	−1.276	1.270
84°	7.704	.014967	.002882	2.35406	2.35427	.89684	1.14540	−.17225	−.7580	−.803	.951	−1.100	1.239
87°	6.698	.015228	.001447	2.49050	2.49074	.47175	.60331	−.20551	−.4006	−1.036	.525	−.636	.764
90°	6.360	.015324	.000000	2.53787	2.53812	.00000	.00000	−.21606	.0000	−1.118	.000	.000	.000
W_6,	cm^{-1}	8.8865	8.8866	13.8952	13.8962	27.01	27.54	28.03	28.81	35.98	45.4	61.0	82.9

These solutions will be either symmetric or antisymmetric at $\varphi=0$ and at $\varphi=\pi/2$, independently; there are thus four symmetry types, which will be designated SS, SA, AS and AA. Several solutions of each type have been computed by the numerical method of Kimball and Shortley,[7] using an interval of 3°. In these solutions we have taken $(1/2\pi)(k/m)^{1/2}=698$ cm^{-1} and then have replaced $\sum W_i$ by the simpler expression

$$1878.8[(1+0.154392\gamma^2-0.162276\gamma^4)^{1/2} -0.996050]\ \text{cm}^{-1}, \quad (43)$$

which is not greatly different from it; the process of solution uses only numerical values in any case, but the use of (43) avoids having to find the roots of (18) and (19) for 31 values of γ. The calculated eigenfunctions and eigenvalues are presented in Table II and Fig. 3; the second column of Table II gives values of the potential energy term (43). The main quantum number characterizing each solution has been taken to be the number of nodes in a period 0 to 2π; the symmetry type is shown as a subscript.

A number of points related to these solutions are worth attention. The lowest level is a very narrow doublet, lying 8.89 cm^{-1} above the potential curve at $\varphi=0$, with a separation of about 1×10^{-4} cm^{-1}, the 0_{SS} level being lower than 2_{SA}; the eigenfunctions for these two states fall off very rapidly as φ increases from 0°; if $\varphi=45°$ is taken as the dividing line, the probability of finding the molecule in the *trans* position is only 8×10^{-4} for 0_{SS} and 7×10^{-4} for 2_{SA}. The second level is again a narrow doublet, 7.54 cm^{-1} above the potential curve at $\varphi=90°$; 2_{AS} is 10×10^{-4} cm^{-1} below 4_{SS}; this is

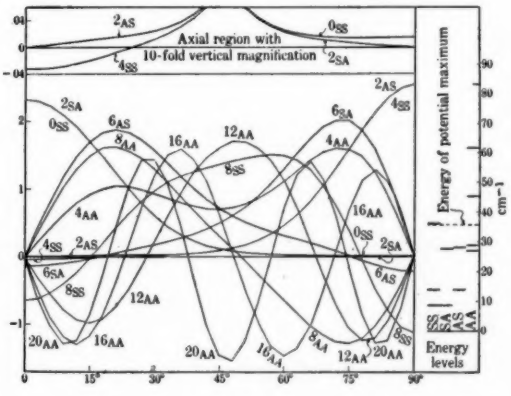

FIG. 3. Rotational eigenfunctions and eigenvalues.

[7] Kimball and Shortley, Phys. Rev. **45**, 815 (1934).

definitely a *trans* state, with a probability of only 5×10^{-4} for the molecule to be found in the *cis* form. 6_{AS} is *cis* and 6_{SA} *trans;* these levels are still quite definitely *vibrational* in character, and have approximately three times the energy of the lowest *cis* and *trans* levels. It is to be expected that 4_{AA} and 8_{AA} will form doublets with these levels; since the latter two levels are of nearly the same energy, however, their would-be doublets, which are of the same symmetry type, can perturb each other. This is seen to occur, and neither 4_{AA} nor 8_{AA} can be characterized as either *cis* or *trans*, although they have far too little energy to execute classical rotations. All higher levels are actually rotating; 8_{SS} barely exceeds the energy of the potential maximum, and hence the eigenfunction is largest in the perpendicular region near $\varphi=\pi/4$. The higher levels execute relatively free rotation.

It is now possible to return to (40) and compute the first-order perturbation energy. It is easily found that for 0_{SS} and 2_{SA}, $W^1=-0.04$ cm^{-1}, while for 2_{AS} and 4_{SS}, $W^1=-0.01$ cm^{-1}. All the other rotational levels of the non-vibrating molecule will have values of this order, the maximum possible being -0.07 cm^{-1}. Thus if the first-order perturbation energy is a reliable criterion, which of course may not be the case, the wave equation is for all practical purposes to be considered separated in the form (29). For higher values of the vibrational quantum numbers, particularly of n_2 and n_5, the perturbation energy will be larger, but it can never exceed $-0.07(n^2+n+1)$ cm^{-1} where n is the largest of the five n_i. This is of the order of 10^{-2} of the anharmonic term for most vibrations and is thus a negligible contribution to the absolute positions of the levels. The change in relative separations of the rotation levels is somewhat more significant, but scarcely serious for moderate values of the quantum numbers.

The form of the pseudo-potential energy curve $\sum W_i$ will be different for each vibrational state. High values of n_1 and n_2 tend to deepen the *trans* minimum and obliterate the *cis* one, while n_4 and n_5 have the reverse effect; values of n_3 of 8 or more would give a shallow minimum near 60°. It is particularly important to note that every set of n_i consisting of four 0's and one 1 gives minima at both the *cis* and the *trans* position, and hence probably has both *cis* and *trans* levels. There should accordingly be absorption bands and Raman lines corresponding to the five frequencies of each of the two plane structures, that is, near 1106, 1100, 1044, 987, 974, 879, 492, 385, 312 and 221 cm^{-1}.

It is possible to make the first-order perturbation energy vanish, by taking

$$A\frac{\partial^2\psi_6}{\partial v_6^2}+B\frac{\partial\psi_6}{\partial v_6}+\frac{2}{h\nu_0}\left\{W_6-\sum_{i=1}^{5}\left[W_i+\frac{n_i^2+n_i+1}{32}\frac{A}{\rho_i^2}\left(\frac{\partial\rho_i}{\partial v_6}\right)^2\right]\right\}\psi_6=0 \qquad (44)$$

instead of (31). This might be desirable if the calculation were to be carried to the second order, but for the present purposes it seemed better to use the obvious form (31) and get a first-order energy which one might hope would give some indication of the accuracy actually obtained.

Frequencies of Plane Forms of C_5

A treatment of the five-carbon chain which attempted as much as has been done for C_4 would be hopelessly difficult. Here there are seven vibrational and two rotational coordinates, and no partial separation into symmetric and antisymmetric coordinates is possible. One would have to expand a ninth order determinant to find the seventh degree equation in λ which determined the frequencies as functions of the two angles and then solve numerically a two-dimensional wave equation to study the rotational motion. It seems likely from the work on C_4, however, that for C_5 also the plane structures will be of outstanding importance, and the vibration frequencies therefore have been calculated for them. There are three such plane structures for C_5, as may be seen in Fig. 4. Two of them, a **W** and a pentagon, have a symmetry axis, and hence give normal modes of

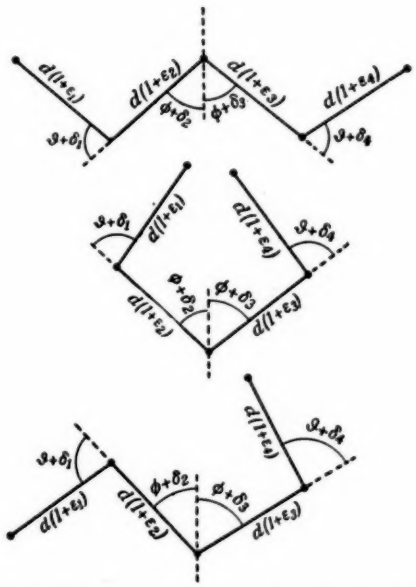

FIG. 4. Coordinates for three plane forms of C_5.

vibration which are either symmetric or antisymmetric; the third form, a dipper, has no helpful symmetry properties, and leads to an unfactored seventh degree determinant. Since the method of calculation is perfectly straightforward, we give only the Hamiltonians and the expanded secular equations. The kinetic energy terms in the Hamiltonian will be useful for a possible subsequent calculation with a more general potential energy.

The original coordinates are shown in Fig. 4. We make the substitutions

$$\begin{aligned} \delta_3+\delta_2&=\eta_1, & \delta_3-\delta_2&=\eta_2,\\ \delta_4+\delta_1&=\eta_3, & \delta_4-\delta_1&=\eta_4,\\ \epsilon_3+\epsilon_2&=\sigma_1, & \epsilon_3-\epsilon_2&=\sigma_2,\\ \epsilon_4+\epsilon_1&=\sigma_3, & \epsilon_4-\epsilon_1&=\sigma_4. \end{aligned} \tag{45}$$

Then for the **W**-form

$$T=(md^2/60)(22\dot\sigma_1^2+18\dot\sigma_1\dot\sigma_3+2^{5/2}\dot\sigma_1\dot\eta_1-12\cdot 2^{1/2}\dot\sigma_1\dot\eta_3+13\dot\sigma_3^2+2^{7/2}\dot\sigma_3\dot\eta_1-2^{5/2}\dot\sigma_3\dot\eta_3+19\dot\eta_1^2+16\dot\eta_1\dot\eta_3$$
$$+11\dot\eta_3^2)+(md^2/636)(70\dot\sigma_2^2+26\dot\sigma_2\dot\sigma_4-2^{5/2}\dot\sigma_2\dot\eta_4+91\dot\sigma_4^2-28\cdot 2^{1/2}\dot\sigma_4\dot\eta_4+41\dot\eta_4^2); \tag{46}$$

for the pentagon form

$$T=(md^2/540)(198\dot\sigma_1^2-30\dot\sigma_1\dot\sigma_3+300\cdot 2^{1/2}\dot\sigma_1\dot\eta_1-156\cdot 2^{1/2}\dot\sigma_1\dot\eta_3+85\dot\sigma_3^2$$
$$-80\cdot 2^{1/2}\dot\sigma_3\dot\eta_1+20\cdot 2^{1/2}\dot\sigma_3\dot\eta_3+395\dot\eta_1^2-400\dot\eta_1\dot\eta_3+131\dot\eta_3^2)$$
$$+(3md^2/1012)(70\dot\sigma_2^2+58\dot\sigma_2\dot\sigma_4-52\cdot 2^{1/2}\dot\sigma_2\dot\eta_4+59\dot\sigma_4^2-36\cdot 2^{1/2}\dot\sigma_4\dot\eta_4+41\dot\eta_4^2); \tag{47}$$

and for the dipper

$$T=(md^2/22{,}860)(7414\dot\sigma_1^2+2464\dot\sigma_1\dot\sigma_2+4730\dot\sigma_1\dot\sigma_3-3184\dot\sigma_1\dot\sigma_4+7112\cdot 2^{1/2}\dot\sigma_1\dot\eta_1-3388\cdot 2^{1/2}\dot\sigma_1\dot\eta_3$$
$$-1720\cdot 2^{1/2}\dot\sigma_1\dot\eta_4+3766\dot\sigma_2^2+1600\dot\sigma_2\sigma_3+658\dot\sigma_2\dot\sigma_4+3556\cdot 2^{1/2}\dot\sigma_2\dot\eta_1-1784\cdot 2^{1/2}\dot\sigma_2\dot\eta_3$$
$$-2660\cdot 2^{1/2}\dot\sigma_2\dot\eta_4+3985\dot\sigma_3^2-880\dot\sigma_3\dot\sigma_4+2540\cdot 2^{1/2}\dot\sigma_3\dot\eta_1-2200\cdot 2^{1/2}\dot\sigma_3\dot\eta_3-820\cdot 2^{1/2}\dot\sigma_3\dot\eta_4$$
$$+3991\dot\sigma_4^2-3556\cdot 2^{1/2}\dot\sigma_4\dot\eta_1+524\cdot 2^{1/2}\dot\sigma_4\dot\eta_3+320\cdot 2^{1/2}\dot\sigma_4\dot\eta_4+11{,}303\dot\eta_1^2-4064\dot\eta_1\dot\eta_3$$
$$-10{,}160\dot\eta_1\dot\eta_4+2453\dot\eta_4^2+1600\dot\eta_3\dot\eta_4+3935\dot\eta_4^2). \tag{48}$$

In each case the potential energy is

$$V=(d^2/4)(k\sigma_1^2+k\sigma_2^2+k\sigma_3^2+k\sigma_4^2+2b\eta_1^2+b\eta_3^2+b\eta_4^2). \tag{49}$$

The secular equations for the **W**-form are

$$\lambda^4-[(11/3)(k/m)+(29/3)(b/m)]\lambda^3+[(29/9)(k^2/m^2)+(247/9)(bk/m^2)+(82/9)(b^2/m^2)]\lambda^2$$
$$-[(41/3)(bk^2/m^3)+(70/3)(b^2k/m^3)]\lambda+10b^2k^2/m^4=0 \tag{50}$$

and

$$\lambda^3-[(13/3)(k/m)+(13/3)(b/m)]\lambda^2+[(41/9)(k^2/m^2)+(161/9)(bk/m^2)]\lambda-(53/3)(bk^2/m^3)=0\,; \quad (51)$$

for the pentagon-form

$$\lambda^4-[(11/3)(k/m)+(29/3)(b/m)]\lambda^3+[(29/9)(k^2/m^2)+31bk/m^2+(82/9)(b^2/m^2)]\lambda^2$$
$$-[(73/3)(bk^2/m^3)+(566/27)(b^2k/m^3)]\lambda+10b^2k^2/m^4=0 \quad (52)$$

and

$$\lambda^3-[(13/3)(k/m)+(13/3)(b/m)]\lambda^2+[(41/9)(k^2/m^2)+(129/9)(bk/m^2)]\lambda$$
$$-(253/27)(bk^2/m^3)=0\,; \quad (53)$$

and for the dipper-form

$$\lambda^7-[8k/m+14b/m]\lambda^6+[(71/3)(k^2/m^2)+(928/9)(bk/m^2)+51b^2/m^2]\lambda^5-[(92/3)(k^3/m^3)$$
$$+(2486/9)(bk^2/m^3)+344b^2k/m^3+(1066/27)(b^3/m^3)]\lambda^4+(1/81)[1189k^4/m^4+25{,}672bk^3/m^4$$
$$+67{,}303b^2k^2/m^4+19{,}664b^3k/m^4]\lambda^3-(1/81)[10{,}550bk^4/m^5+68{,}156b^2k^3/m^5+42{,}838b^3k^2/m^5]\lambda^2$$
$$+(1/81)[24{,}079b^2k^4/m^6+38{,}312b^3k^3/m^6]\lambda-(1270/9)(b^3k^4/m^7)=0. \quad (54)$$

This last equation comes from an unfactorable seven-rowed determinant which might appear impossibly laborious to expand; by suitable manipulation, however, it is possible to reduce the determinant one row at a time, always retaining somewhere a monomial term with which a row of zeros can easily be produced; the expansion in this way requires only three or four hours.

When $b/k=0.1$ and $(1/2\pi)(k/m)^{1/2}=698$ cm^{-1}, the frequencies are as given in Table III.

TABLE III.

W-form	Pentagon-form	Dipper-form
1041	1092	1126
1008	853	1062
336	559	995
213	143	908
1115	1127	467
946	981	343
428	298	174

The first four frequencies for the **W**- and pentagon-forms belong to symmetrical, the last three to antisymmetrical, vibrations.

COMPARISON WITH EXPERIMENT

There are no data on the fine structure of absorption or of Raman lines which could be compared with the calculated torsional and low rotational levels of the φ-motion. Such a comparison would in any case be difficult without knowledge of the selection rules, which we have not found, and without any theoretical study of the states with nonvanishing total angular momentum. Hence it is only possible to seek necessarily rough correspondences between calculated vibration frequencies and the observed spectra. The choice $b/k=0.1$ has been found to give the best results; Fig. 5 shows the calculated frequencies for C_2, C_3, C_4 and C_5, and such experimental data as are available for ethane, propane, butane and pentane.

The C–C frequency for ethane is definitely located at 993 cm^{-1} by the Raman data of Bhagavantam[8] and Lewis and Houston.[9] The infrared line at 838 cm^{-1} reported by Coblentz[10] cannot be understood, since it seems too low to be a C–H bending frequency. The Raman data on propane are from Bhagavantam and Kohlrausch and Köppl,[11] the infrared from Bartolome;[12] an infrared line at 750 cm^{-1} which is tentatively identified as the harmonic of the Raman line at 373 cm^{-1} has accordingly been

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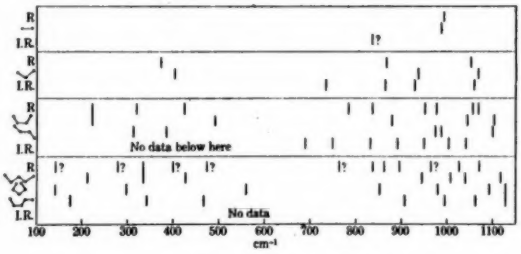

FIG. 5. Calculated and observed frequencies.

omitted from the figure. The Raman data on butane are due to Bhagavantam, Murray and Andrews[13] and Kohlrausch and Köppl, while the infrared are from the old work of Coblentz. In the case of pentane, twelve Raman lines below 1100 cm^{-1} were reported by Ganeswan and Venkateswaran,[14] a number of which have not been confirmed by the later work of Kohlrausch and Köppl and are indicated as doubtful. No infrared data are available for pentane. The calculated deformation frequencies for the pentagon form are certainly worthless due to the repulsion between the terminal CH_3 groups.

When allowance is made for the extreme approximations of the theory, and the uncertainty of the experimental data, there does seem to be a fairly satisfactory statistical agreement between the two. One may therefore feel that the frequencies calculated for still longer chains will be approximately correct and can be used to estimate specific heats and other thermodynamic properties without gross errors. It is intended to do this in the near future.

ACKNOWLEDGMENT

The author is very grateful to Dr. C. W. Montgomery for his assistance in making and checking the various calculations of this paper.

APPENDIX. THE KINETIC ENERGY OF A ROTATING MOLECULE

Treatises on mechanics give the rotational energy of a rigid body in terms of moments of momentum about the principal axes. A more general formula is derived here. Let the moments and products of inertia be

$$\begin{aligned} A&=m\sum(y^2+z^2), \quad B=m\sum(x^2+z^2),\\ C&=m\sum(x^2+y^2), \quad D=m\sum yz,\\ E&=m\sum xz, \quad\quad F=m\sum xy, \end{aligned} \tag{55}$$

and the instantaneous moments of momentum be

$$\begin{aligned} M_x&=m\sum(\dot{y}z-\dot{z}y), \quad M_y=m\sum(\dot{z}x-\dot{x}z),\\ M_z&=m\sum(\dot{x}y-\dot{y}x). \end{aligned} \tag{56}$$

It is supposed that the origin of the system is fixed at the center of gravity. Transform to rotating axes by the infinitesimal rotation

$$\begin{aligned} x&=X-\epsilon_z Yt+\epsilon_y Zt, \quad X=x+\epsilon_z yt-\epsilon_y zt,\\ y&=\epsilon_z Xt+Y-\epsilon_x Zt, \quad Y=-\epsilon_z xt+y+\epsilon_x zt,\\ z&=-\epsilon_y Xt+\epsilon_x Yt+Z, \quad Z=\epsilon_y xt-\epsilon_x yt+z, \end{aligned} \tag{57}$$

where t is at once the time and an infinitesimal parameter. Setting the moments of momentum in the new coordinate system equal to zero gives the conditions

$$\begin{aligned} A\epsilon_x-F\epsilon_y-E\epsilon_z&=-M_x,\\ -F\epsilon_x+B\epsilon_y-D\epsilon_z&=-M_y,\\ -E\epsilon_x-D\epsilon_y+C\epsilon_z&=-M_z. \end{aligned} \tag{58}$$

It is then easily shown that

$$\begin{aligned} T_{\text{rot}}&=(m/2)\sum(\dot{x}^2+\dot{y}^2+\dot{z}^2)\\ &\quad-(m/2)\sum(\dot{X}^2+\dot{Y}^2+\dot{Z}^2)\\ &=-(1/2)(\epsilon_x M_x+\epsilon_y M_y+\epsilon_z M_z)\\ &=(1/2)[(BC-D^2)M_x^2+(AC-E^2)M_y^2\\ &\quad+(AB-F^2)M_z^2+2(CF+DE)M_xM_y\\ &\quad+2(BE+DF)M_xM_z+2(AD+CF)M_yM_z]\\ &\quad\times[ABC-AD^2-BE^2-CF^2-2DEF]^{-1}. \end{aligned} \tag{59}$$

When only one product of inertia, say E, is not zero, the result reduces to

$$\begin{aligned} T_{\text{rot}}&=(1/2)[M_y^2/B+(CM_x^2+2EM_xM_z\\ &\quad+AM_z^2)/(AC-E^2)], \end{aligned} \tag{60}$$

which is the form needed in this paper.

[13] Murray and Andrews, J. Chem. Phys. **1**, 406 (1933).
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The Free Energy of Sulphur Dioxide

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Values of $(F°-E°_0)/T$ for sulphur dioxide are computed from spectroscopic data; the heat of formation of sulphur dioxide from diatomic sulphur and oxygen is calculated from the calorimetric heats of formation of sulphur dioxide and hydrogen sulphide, and Cross' value for the energy of dissociation of hydrogen sulphide. Equilibrium constants for the reactions

$$\tfrac{1}{2}S_2(g)+O_2=SO_2, \qquad SO+\tfrac{1}{2}O_2=SO_2$$

are tabulated for the range 298.1 to 2800°K.

OF all the simpler gases the one which presented the greatest experimental difficulties in the determination of its free energy was probably sulphur dioxide. There was no appreciable dissociation at any attainable temperature, and the only values of its free energy of formation have been determined indirectly from other equilibria.[1, 2, 3] The success that has attended the use of spectroscopic data in predicting equilibrium constants for other reactions suggests that the same method might be used for sulphur dioxide, although in this case the data are not as complete as one could wish.

For SO_2 the constants[4] are: A, B, $C=12.3$, 73.2, 85.5×10^{-40}; $\nu(\sigma)=1378-8\nu_\sigma$, $\nu(\pi)=1150$, $\delta=520$ cm^{-1}. Ionescu gives no details of his rotational analysis, but his moments of inertia are consistent with Kohlrausch's value[5] of the valence angle (119° 40′) and with Wierl's value[6] for the S–O distance (1.37A). The resulting $(F°-E°_0)/T$ are given in the second column of Table I. Since $(F°-E°_0)/T$ is known for sulphur vapor[7] and for oxygen,[8] the only additional information that is needed for a calculation of equilibria involving SO_2 is the value of $\Delta E°_0$ or of ΔH_{298} for the reaction $\frac{1}{2}S_2(g)+O_2=SO_2$.

TABLE I. $K_1=(P_{SO_2})/(P_{S_2})^{1/2}(P_{O_2})$; $K_2=(P_{SO_2})/(P_{SO})(P_{O_2})^{1/2}$.

T°K	$-(F°-E°_0)/T$	log K_1	log K_2	T°K	$-(F°-E°_0)/T$	log K_1	log K_2
298.1	50.56	59.65	54.53	900	60.89	17.17	15.28
300	50.62	59.25	54.16	1000	62.01	15.06	13.34
350	51.93	50.24	45.84	1200	64.00	11.91	10.42
400	53.10	43.48	39.60	1400	65.73	9.65	8.33
500	55.11	34.02	30.85	1600	67.27	7.96	6.77
600	56.83	27.70	25.01	2000	69.92	5.60	4.59
700	58.33	23.19	20.84	2400	72.15	4.02	3.13
800	59.67	19.80	17.72	2800	74.06	2.90	2.09

Eckman and Rossini[9] have measured the heat of combustion of rhombic sulphur ($\Delta H_{298}=-70{,}940\pm50$ cal.) but thermal data for the reaction $S(rh)=\frac{1}{2}S_2(g)$ are unknown. These can be obtained, however, with sufficient accuracy for the purpose in hand from the recent calculation of Cross[10] for the hydrogen sulphide dissociation based on his rotational analysis of the hydrogen sulphide spectrum,[11] and the determination by Zeumer and Roth[12] of the heat of formation of hydrogen sulphide from rhombic sulphur and hydrogen ($\Delta H_{298}=-4800\pm150$ cal.). Cross finds for the reaction $H_2+\frac{1}{2}S_2(g)=H_2S$, $\Delta E°_0=-19{,}620$ cal.; from this, and the spectroscopic free energies of hydrogen sulphide,[10] sulphur[13] and hydrogen,[14] $\Delta F°_{298.1}=-17{,}570$ cal. and since $S°_{298.1}$ for H_2S, S_2 and H_2 is 49.15, 54.42 and 31.23, respectively, ΔH_{298} is $-20{,}340$ cal. Com-

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[2] Randall and Bichowsky, J. Am. Chem. Soc. **40**, 368 (1918).
[3] Ferguson, J. Am. Chem. Soc. **40**, 1626, 1900 (1918).
[4] Ionescu, Comptes rendus **196**, 1476 (1933); Smyth, Phys. Rev. **44**, 690 (1933). The universal constants used in the calculations of this paper are: $h=6.554\times10^{-27}$, $k=1.372\times10^{-16}$, $c=2.9986\times10^{10}$, $R=1.9869$, additive constant for the translational free energy $=-7.267$.
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[13] In the calculations of this paper, Montgomery and Kassel's values of $-(F°-E°_0)/T$ (reference 7) have been increased by 0.55 cal./degree as recommended by Cross (reference 10).
[14] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

bining this value with Zeumer and Roth's result, it follows that ΔH_{298} for the reaction $S(rh) = \frac{1}{2}S_2(g)$ is 15,540 cal., and consequently ΔH_{298} for the reaction $\frac{1}{2}S_2(g)+O_2=SO_2$ is $-86{,}480$ cal. Since $S^\circ_{298.1}$ for oxygen[8] and for sulphur dioxide is 49.02 and 59.02, respectively, $\Delta F^\circ_{298.1}$ for the formation of SO_2 from diatomic sulphur and oxygen is $-81{,}350$ cal. and ΔE°_0 is $-85{,}860$ cal.

There is an alternative method of obtaining the heat of vaporization of diatomic from rhombic sulphur similar to that used by Lewis and Randall.[15] For the four reactions

$H_2S = H_2 + \frac{1}{2}S_2(g)$, $\Delta F^\circ_{298.1} = 17{,}570$ cal.,
$2HI + S(rh) = H_2S + I_2(s)$, " $= -8470$ cal.,[16]
$H_2 + I_2(g) = 2HI$, " $= -3690$ cal.,[17]
$I_2(s) = I_2(g)$, " $= 4620$ cal.[18]

Hence for the reaction $S(rh) = \frac{1}{2}S_2(g)$, $\Delta F^\circ_{298.1} = 10{,}030$ cal., and, since the third law entropy of rhombic sulphur is 7.69 cal./degree,[19] ΔH_{298} for this reaction is 15,850 cal., which agrees with the previous result (15,540 cal.) probably as closely as can be expected.

In the third column of Table I are given the values[20] of $\log K_1 = \log (P_{SO_2})/(P_{S_2})^{\frac{1}{2}}(P_{O_2})$, computed from the spectroscopic values of $(F^\circ - E^\circ_0)/T$ for the constituents, on the assumption that ΔE°_0 for the reaction is $-85{,}860$ cal. In the last column are the equilibrium constants for the "sulphur monoxide" dissociation of SO_2, $\log K_2 = \log (P_{SO_2})/(P_{SO})(P_{O_2})^{\frac{1}{2}}$; these were obtained by means of Montgomery and Kassel's table of $(F^\circ - E^\circ_0)/T$ for SO, on the assumption that ΔE°_0 for the reaction $SO + \frac{1}{2}O_2 = SO_2$ is $-79{,}300$ cal. It is evident that the equilibrium constant for the reaction $\frac{1}{2}S_2(g) + SO_2 = 2SO$, is given by the relation $\log (P_{SO})^2/(P_{S_2})^{\frac{1}{2}}(P_{SO_2}) = \log K_1 - 2 \log K_2$.

Of the equilibria involving SO_2 which have been studied experimentally, Randall and Bichowsky's measurements[2] for the reaction $SO_2 + 3H_2 = 2H_2O + H_2S$ and Ferguson's[3] for the reaction $SO_2 + 2CO = \frac{1}{2}S_2(g) + 2CO_2$ can be compared with the results of calculation. For the former, from Rossini's value[21] for the heat of formation of steam, ΔE°_0 for the reaction is $-47{,}980$ cal.; from this and the known free energies of hydrogen,[14] steam[22] and hydrogen sulphide,[10] $\log (P_{H_2O})^2(P_{H_2S})/(P_{SO_2})(P_{H_2})^3$ for 1160°, 1362°, 1473° and 1645°K is 5.58, 4.06, 3.40 and 2.54, respectively. Randall and Bichowsky found for the same four temperatures 5.93, 4.32, 3.54 and 2.56. Calculation shows that the amount of sulphur monoxide present under the conditions of their experiments is quite negligible, and also (from the data of Montgomery and Kassel) that the dissociation of diatomic into monatomic sulphur can likewise be ignored. There is thus a discrepancy of about 1.6 cal./degree in $R \ln K$ at the lowest of their temperatures, this difference decreasing rapidly as the temperature rises. This improvement in the agreement is perhaps significant, since one would expect *caeteris paribus* that equilibrium would be the more readily established the higher the temperature. It should be noted in passing that the revised free energy equation of Eastman[23] for SO_2 combined with the spectroscopic free energies of formation of H_2O and H_2S gives for $\log K$ at the same four temperatures, 6.50, 4.97, 4.30 and 3.43—definitely in worse agreement with Randall and Bichowsky's results than are those obtained above.

For the second reaction, studied by Ferguson, from Rossini's heat of combustion of carbon monoxide[24] and the spectroscopic free energies,[25] $\log (P_{SO_2})(P_{CO})^2/(P_{S_2})^{\frac{1}{2}}(P_{CO_2})^2$ for 1275° and 1460°K is -3.07 and -2.02, respectively; Ferguson found -3.56 and -2.38. The disagreement between the results of calculation and experiment is thus definitely greater than the apparent uncertainty in the experimental data (± 0.2 in $\log K$) on the one hand and in the calculated thermodynamic quantities on the other, although here again the discrepancy decreases with rise in temperature.

[15] Lewis and Randall, *Thermodynamics*, 1923, p. 540 *et seq.*
[16] Pollitzer, Zeits. f. anorg. Chemie **64**, 121 (1909).
[17] Zeise, Zeits. f. Elektrochemie **40**, 885 (1934).
[18] Baxter, Hickey and Holmes, J. Am. Chem. Soc. **29**, 127 (1907); Giauque, J. Am. Chem. Soc. **53**, 507 (1931).
[19] Int. Crit. Tab. **5**, 89.
[20] A preliminary table of $\log K_1$ is given in a recent review article by Zeise, Zeits. f. Elektrochemie **40**, 885 (1934). The values given there differ slightly from those of this paper, since at that time Cross' calculations for hydrogen sulphide had not appeared.
[21] Rossini, Bur. Standards J. Research **6**, 1 (1931).
[22] Gordon, J. Chem. Phys. **2**, 65, 549 (1934).
[23] Eastman, Bur. Mines Infor. Circ. No. 6454 (1931).
[24] Rossini, Bur. Standards J. Research **6**, 37 (1931).
[25] For CO, Clayton and Giauque, J. Am. Chem. Soc. **55**, 5071 (1933); for CO_2, Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).

The Mercury Photosensitized Polymerization of Acetylene and Acetylene-d_2

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The mercury photosensitized polymerization of acetylene and acetylene-d_2 has been studied. The rate of reaction is 30 percent greater with acetylene than with the deutero-compound, over the whole pressure range investigated. At low pressures, the rate varies as the acetylene pressures but in the pressure range 0.7–4 cm the initial rate of polymerization is practically independent of the acetylene pressure and determined by the intensity of absorbed resonance radiation. The quantum yield is approximately 6.5 for acetylene and 5 for acetylene-d_2 lower than the yield for acetylene at the same temperature in the photochemical reaction ($\lambda \sim 2000$A). The results are also compared with corresponding studies of the polymerization process under the influence of α-particles.

WE have applied the technique developed by us in our studies of the mercury photosensitized decomposition of the deuteroammonias[2] to a comparison of the polymerization of acetylene and acetylene-d_2 under the influence of excited mercury. Bates and Taylor[3] indicated qualitatively that acetylene could be polymerized to solid cuprene under such conditions. The straight photochemical polymerization of acetylene has already been studied by Lind and Livingston[4] who have determined the influence of pressure and temperature and the quantum yield, this latter being compared with the ion yield in the parallel determinations of polymerization under the influence of α-particles.[5] One of us (J.C.J.) has already, in collaboration with Lind, compared the rates of polymerization of acetylene and acetylene-d_2 under the influence of α-particles and found that these rates were identical within the error of experiment.[6] It was of interest to ascertain whether this identity of reaction rates extended to the reactions induced by light.

Apparatus

The experiments were carried out with the apparatus already described by us in our record of the work on the deuteroammonias.[2] The quartz reaction-vessel there employed was very suitable also in the present work owing to the device employed for increasing the sensitivity of the pressure measurements which were made after compression of the reacting gases to a small volume. This permitted us to study accurately small amounts of polymerization at relatively low pressures and thus to avoid the difficulties attendant on photochemical experiments in which opaque deposits of product form on the reaction vessel. As source of resonance radiation we again employed the Hanovia quartz mercury vapor, rare gas discharge tube, Sc–2537, operating at 5000 volts from the 110-volt a.c. lighting circuit through a 30-milliampere transformer. The advantages of this type of tube have already been described.[2] We used the radiation transmitted through a quartz cell containing 25 percent acetic acid, 1.5 cm in thickness which eliminated the short wavelength light that is photochemically active, but which transmits the resonance radiation. Between each experiment, the quartz reaction vessel was cleaned by heating it in the presence of oxygen.

Materials

The samples of acetylene and acetylene-d_2 were prepared by interaction of the vapors of water and of pure deuterium oxide ($d_{25}^{25} = 1.1079$) with samples of pure calcium carbide. This carbide was placed at our disposal by the Union Carbide and Carbon Research Laboratories, Inc., through the courtesy of Dr. C. E. MacQuigg. The sample which the donor believed to be quite pure was entirely different in outward appearance from commercial products. It was nut-brown in color and was preserved in a moisture-proof can. For the preparations, the inner cores of freshly broken lumps were chosen, introduced into the

[1] C.R.B. Fellow from Louvain University, 1934–35.
[2] Jungers and Taylor, J. Chem. Phys. **2**, 373 (1934).
[3] Bates and Taylor, J. Am. Chem. Soc. **49**, 2444 (1927).
[4] Lind and Livingston, J. Am. Chem. Soc. **54**, 94 (1932).
[5] Mund and Koch, Bull. Soc. Chim. Belg. **34**, 125, 241 (1925); Lind and Bardwell, J. Am. Chem. Soc. **48**, 1556 (1926).
[6] Lind, Jungers and Shiflett, Phys. Rev. **46**, 825 (1934).

preparation vessel, heated and exhausted in vacuum at 400°C for 24 hours before reaction with the water vapors. The products were condensed in liquid air and the middle fractions only used for experimental work. We cite the data of Glockler and Davis,[7] on the Raman spectrum of our acetylene-d_2 preparation as evidence of its distinctive characteristics as compared with acetylene and acetylene-d_1.

Experimental Results

The rates of polymerization of the two acetylenes, at pressures of 0.1, 0.25, 0.7 and 4 cm, are shown graphically in Fig. 1. The measurements were made at room temperatures (*ca.* 25°C) with the gases confined over mercury and hence saturated with mercury vapor at that temperature. It is immediately evident that, over the pressure range employed, the rate of acetylene polymerization is always greater than that of the acetylene-d_2. Computation shows that, at each pressure, the rate, in the case of the light acetylene, is 30 percent greater than that of the heavy acetylene. The curves at the lowest pressure represent approximately 90 percent total reaction. At the higher pressures the change is not followed so far. It is also evident that, at the lower pressures, the initial rate of polymerization is strongly dependent on the pressure, but the data at the higher pressures show that the rate has become practically independent of the acetylene pressure. This pressure dependence is undoubtedly governed by the effectiveness of the acetylenes in taking up the energy of the excited mercury and reveals that there is no essential difference between the two acetylenes in this respect. In the higher pressure range the rates are therefore determined by the concentration of excited mercury

$$-d(C_2H_2)/dt = k[Hg'],$$
$$-d(C_2D_2)/dt = k[Hg'].$$

The available intensity of resonance radiation was ascertained by measurement of the rate of reaction of an electrolytic gas mixture ($2H_2+O_2$) under identical operating conditions. It was found that the rate of polymerization of acetylene

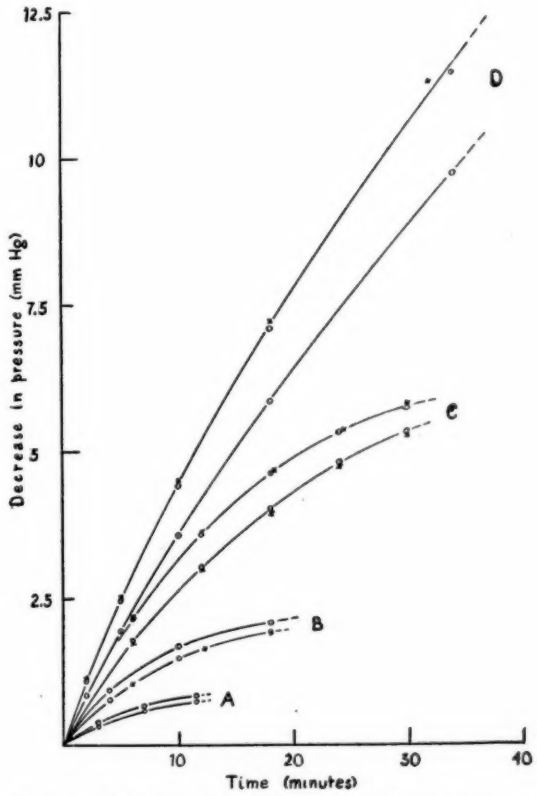

Fig. 1. Velocity of polymerization of acetylene and acetylene-d_2 at (A) 0.11, (B) 0.25, (C) 0.7 and (D) 4 cm initial pressure.

in the high pressure range was approximately 30 percent greater than that of the hydrogen-oxygen reaction under the same conditions of illumination and mercury pressure. Since the quantum yield in this latter reaction is found to be less than $3H_2O_2$ per quantum[8] or approximately 5 molecules of hydrogen plus oxygen disappearing, we assign a quantum yield of not more than 6.5 to the photosensitized polymerization of acetylene and a 30 percent lower yield, or approximately 5 molecules per quantum for heavy acetylene.

Discussion

The experiments which we have performed serve still further to differentiate the polymerization of the acetylenes under the action of ions

[7] Glockler and Davis, Phys. Rev. **46**, 535 (1934).

[8] Marshall, J. Phys. Chem. **30**, 34, 1078, 1634 (1926); J. Am. Chem. Soc. **45**, 4460 (1932). Frankenburger and Klinkhardt, Zeits. f. physik. Chemie **8**, 138 (1930); **15**, 421 (1932).

and of light. Whereas with the former (α-particles), there is no difference in the rates of polymerization with the heavy and light molecules, in the present work the heavy acetylene polymerizes at a markedly slower rate under the same intensity of excited mercury. There is a progression, also, in the yield of the respective processes. Under the influence of β-particles,[9] 26 molecules of acetylene polymerize per ion pair. With α-particles the rate of disappearance of the two acetylenes is 18–20 molecules per ion pair[10] practically independent of temperature. Lind and Livingston found a value for the photochemical polymerization ($\lambda \sim 2000$A) of 9.5 molecules per quantum at 25°C and values varying from 7 to 11 per quantum in the temperature range of 7–40°C, with the temperature coefficient of 1.25 per 10° increase in temperature responsible for this variation, the absorption coefficient being temperature independent within the limits of accuracy of the measurements. With the smaller quantum of light energy involved in the photosensitized polymerization ($\lambda = 2537$A), the quantum yield falls still further to 6.5 molecules per quantum at 25°C.

All these data point to the conclusion that the polymerization process in the case of the acetylenes rapidly dissipates the energy which is employed to initiate the process. With agents such as α-particles, β-particles and cathode rays the chain mechanism is most pronounced and the velocities of polymerization identical in the case of light and heavy acetylenes. In the case of acetylene radiated by α-particles it is known that the only observable effect of temperature is slightly negative (2 percent in 100°) and this has been explained on the basis of decreasing capture of molecules by the charged particle with increase in temperature.[11] We conclude that the electrostatic attraction of the charged particles produced by the radiation determines the magnitude of the ion yield and serves in place of the activation energy of collision necessary where such attractive forces are absent. With less energetic agents such as light, temperature activation is a markedly contributory factor, the evidence indicating that the heavy acetylene requires greater thermal activation for the chain process. In this respect, there is a possibility that the exchange of energy between excited mercury and acetylene-d_2 is not so efficient as with acetylene. The absence of pressure effect at the higher pressures makes this, however, appear improbable. The effect of temperature as an auxiliary agent cannot be followed into the higher temperature ranges since it is known that in the region of 250°C the product is no longer cuprene, a complex of products, including benzene, being formed.[12] In the thermal polymerization process, which requires an activation energy of the order of 40,000 calories,[13] cuprene is also not produced but a complex mixture of products. All these polymerization processes as well as those of methyl acetylene and allene[14] appear to involve only short chains, in contrast to the polymerization of styrene and vinyl acetate in which the chain length may reach thousands of molecules per quantum absorbed.[15]

[9] Mund and Jungers, Bull. Soc. Chim. Belg. **40**, 158 (1931).

[10] An explanation for this lower yield with α-particles has already been put forward by Mund and Jungers, reference 9. Recombination of ions, due to their greater concentration in the path of the α-particle, may account for the lower value as compared with β-particles.

[11] Mund, Ann. Soc. Sci. Brussels **B54**, 30 (1934).

[12] Kato, Bull. Inst. Phys. Chem. Res. (Tokyo) **10**, 343 (1931); Kemula and Mrazek, Zeits. f. physik. Chemie **B23**, 358 (1933); Livingston and Shiflett, J. Phys. Chem. **38**, 377 (1934).

[13] Pease, J. Am. Chem. Soc. **51**, 3470 (1929).

[14] Lind and Livingston, J. Am. Chem. Soc. **55**, 1036 (1933).

[15] Taylor and Vernon, J. Am. Chem. Soc. **53**, 2527 (1931).

The Ethane-Ethylene-Hydrogen Equilibrium*

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An attempt has been made to correlate several data on this system by a statistical calculation of the equilibrium constants in the temperature range of 400 to 700°C. The data are in good agreement but the calculated values of the K's are smaller than the experimental by a factor of two. It is thought that the principal reason for this discrepancy lies in the calculation of the entropy of free rotation in ethane, although other factors may contribute.

THERE are in existence two fairly recent determinations of the equilibrium constants of the ethane-ethylene-hydrogen system. The first is that of Pease and Durgan,[1] who, using a static system and approaching the equilibrium from both sides, found K's at 600°, 650° and 700°C. The other, which is the work of Frey and Huppke,[2] was carried out in a flow system by catalytic dehydrogenation of ethane at one atmosphere pressure in the temperature range from 400–500°C. The results of these two researches are in good agreement.[3] The purpose of this paper is to attempt to correlate by means of statistical calculations the figures obtained from these experiments with the recent accurate measurement of the heat of hydrogenation of ethylene at 82°C as determined by Kistiakowsky *et al.*[3]

For the present calculation the values of the entropy (excluding nuclear spin) and of the heat content of hydrogen at the desired temperatures have been taken by direct graphical interpolation of the data of Davis and Johnston.[4]

There are in the literature several recent discussions of the computation of the entropy of polyatomic molecules such as ethylene and ethane.[5] It suffices for the present paper to give briefly the specific values and assumptions actually used.

The calculation of the translational entropies of ethane and ethylene requires no discussion; the values obtained are given in Table II. The estimation of the magnitude of the vibrational entropies is, however, a somewhat more difficult matter. Neither of these molecules has been completely analyzed. In the case of ethylene Kassel[4a] has lumped Mecke's[6] eleven frequencies in the following manner: 950 cm^{-1} (triple); 1100 (single); 1400 (double); 1620 (single); and 3090 (quadruple). Kassel assumes for the frequency of the torsion about the double bond the value of 950 cm^{-1}. Penney,[7] however, gives 750 cm^{-1} (a figure quoted to him verbally by Sutherland). In view of the uncertainty of this frequency it was decided to select 790 cm^{-1} which gives the best agreement with the accurate experimental values of Cp for ethylene as determined by Eucken and Parts,[8] as shown by Table Ia. It is seen that the figures deviate but slightly and in a random manner over quite a

TABLE I.

(a)

Ethylene: vibrational heat capacity (12 degrees of freedom)

T	143	160	196	245	280	373.5	464
$\Sigma C_{vib.}$(calc.)	0.092	0.183	0.540	1.347	2.078	4.164	5.914
$C_{vib.}$(E. & P.)*	0.08	0.21	0.53	1.30	2.03	3.96	6.20
Deviation	+0.01	−0.03	+0.01	+0.05	+0.05	+0.20	−0.29

* $8R/2$ has been deducted from the Cp values of Eucken and Parts.

(b)

Ethane: vibrational heat capacity (17 degrees of freedom)

T	143	160	196	245	280	373.5
$\Sigma C_{vib.}$(calc.)	0.242	0.434	1.043	2.224	3.211	6.068
$C_{vib.}$(E. & P.)*	0.32	0.50	1.16	2.13	3.18	5.89
Deviation	−0.08	−0.07	−0.12	+0.09	+.03	+0.18

* $9R/2$ has been deducted from the Cp values of Eucken and Parts.

* Presented at the N. Y. meeting of the Am. Chem. Soc., 1935.

[1] Pease and Durgan, J. Am. Chem. Soc. **50**, 2715 (1928).

[2] Frey and Huppke, Ind. Eng. Chem. **25**, 54 (1933).

[3] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65 (1935).

[4] Davis and Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).

[5] See for example (a) Kassel, J. Am. Chem. Soc. **55**, 1361 (1933); (b) Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933); (c) Halford, J. Chem. Phys. **2**, 694 (1934). This latter paper gives the formulae quite explicitly.

[6] Mecke, Zeits. f. physik. Chemie **B17**, 1 (1932).

[7] Penney, Proc. Roy. Soc. **A144**, 166 (1934).

[8] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 190 (1933).

TABLE II.

T	298°	355	673	773	873	973
(a) Entropy of ethylene						
Translational	35.968	36.833	40.018	40.706	41.307	41.848
Vibrational	0.671	1.233	5.761	7.305	8.831	10.320
Rotational	15.909	16.439	18.349	18.759	19.119	19.439
Total	52.548	54.505	64.128	66.770	69.257	71.607
(b) Entropy of ethane						
Translational	36.175	37.040	40.225	40.913	41.514	42.055
Vibrational	1.149	1.950	8.106	10.220	12.320	14.390
Rotational	18.903	19.602	22.146	22.694	23.180	23.611
Total	56.227	58.592	70.477	73.827	77.014	80.056
(c) Entropy of hydrogen						
Total	31.230	32.420	36.905	37.873	38.473	39.517
(d)						
ΔS for $H_2+C_2H_4\rightarrow C_2H_6$	−27.551	−28.333	−30.556	−30.816	−30.986	−31.068
(e) Heat content						
H_2	2023	2417	4642	5348	6057	6775
C_2H_4	2534	3171	8062	9976	12,025	14,197
C_2H_6	2939	3713	9768	12,195	14,822	17,625
(f) ΔH for $C_2H_4+H_2\rightarrow C_2H_6$	−32,567	−32,824±50	−33,885	−34,078	−34,209	−34,296
(g) ΔF for $C_2H_4+H_2\rightarrow C_2H_6$	−24,358	−22,767	−13,322	−10,255	−7157	− 4069
(h) K calc.	$7.08(10^{19})$	$1.01(10^{16})$	$2.10(10^{6})$	$7.89(10^{2})$	61.7	8.19
(i) $1/K$ (calc.)*			0.000048	0.0013	0.016	0.122
(j) K of $C_2H_6\rightarrow C_2H_4+H_2$ (obs.)			0.00015[2]	0.0032[2]	0.031[1]	0.20[1]
(k) K of $C_2H_6\rightarrow C_2H_4+H_2$ (recalc.)†			0.000083	0.0024	0.031	0.17

* or K for the reaction written $C_2H_6\rightarrow C_2H_4+H_2$.
† as done by Kistiakowsky *et al.*; see reference 3.

large temperature range. Ethane has been treated in similar fashion using the assignments of Eucken and Parts; namely, 712 cm^{-1} (double); 826 (double); 990 (single); 1460 double; 1465 (double); 1499 (double); and 2975 (sixfold); a total of seventeen vibrational degrees of freedom. The results obtained with these assignments are given in Table Ib. Use of these two sets of frequencies gives the values for $S_{vib.}$ to be found in Table II. The entropy of nuclear spin has been omitted in all calculations.

After a consideration of the various interatomic distances given by different authors, the following values were chosen for the calculation of the moments of inertia of the two hydrocarbons: C−C, 1.53A; C=C, 1.36; C−H, 1.08. The tetrahedral angle was assumed in the case of ethane, and the angle between the two carbon-hydrogen linkages on either end of the ethylene molecule was taken to be 110 degrees. This latter value is probably incorrect, but is sufficiently accurate for the present work. The moments of inertia found for ethylene were 5.205 (10^{-40}), 29.53 (10^{-40}) and 34.71 (10^{-40}). Those used in the case of ethane were 10.27 (10^{-40}) and 35.98 (10^{-40}) (double). A symmetry number of four was used in obtaining the values for $S_{rot.}$ of ethylene as given in Table IIa.

The free rotation of the two methyl groups in ethane complicates the statistical computation of its entropy of rotation. Eucken and Weigert[9] found their values of Cp for ethane to be in accord with the quantum-mechanical treatment of this problem as analyzed by Teller and Weigert.[10] The latter showed that this contribution to the rotational heat capacity becomes classical at 298°K, going through a slight "hump" in approaching this temperature. If one calculates the rotational entropy assuming free rotation to lowest temperatures (using two pairs of moments of inertia; namely, 5.14 (10^{-40}) and 35.98 (10^{-40}), and a symmetry number of 18), he obtains the data given in Table IIb.

That the assumption of free rotation to lowest temperatures is permissible may be shown in the following manner. If C (of internal rotation) as obtained from the paper of Teller and Weigert is plotted against ln T, graphical integration

[9] Eucken and Weigert, Zeits. f. physik. Chemie **B24**, 277 (1934).
[10] Teller and Weigert, Nachr. d. Ges. d. Wiss. zu Göttingen, 218 (1933).

gives the contribution to the rotational entropy at any temperature. This area was found to correspond to 7.241 e. u. at 298°K. The classical calculation of this portion of $S_{rot.}$ (setting $\sigma=9$) gives the value of 7.160 e. u. These values are in reasonable agreement.

The heat contents of Table IIc were arrived at by use of the vibrational frequencies already mentioned, together with the assumption that rotation has already become classical at these temperatures. The value of ΔH for the reaction

$$H_2+C_2H_4\rightarrow C_2H_6$$

on which the final data are based is $-32{,}824$ ± 50 cal. at 355°K.[3] The summary of the calculations is shown in the last few lines of the listing.

It is immediately apparent that the three researches are essentially in agreement. However, the calculated values of $1/K$ are fairly uniformly one-half as large as the experimental figures for the equilibrium constant. This discrepancy presents a real problem. To decrease the $K_{calc.}$ (line *h*) by a factor of two would necessitate a change of ΔH beyond probability. At 298°K such an alteration would involve a change in ΔS of 1.376 e. u., and so would decrease the original difference in the entropy of ethane and ethylene from 3.7 to 2.3 e. u. This latter figure agrees well with the empirical rule of Parks and Huffman[11] that the entropy difference between a saturated hydrocarbon and its corresponding olefine is 2.7 e. u. at 298°K.

An attempt to localize this difference of 1.38 e. u. in some part of the entropy calculation results in the elimination of $S_{trans.}$. It likewise seems improbable that there is any large error in the estimation of $S_{vib.}$ for the two hydrocarbons; indeed the contributions from this type of motion are small at 298°K and are undoubtedly of correct relative magnitudes. It is possible, however, that at higher temperatures this calculation may be in error. However, the inconsistency may more probably be attributed to $S_{rot.}$. The configuration given ethylene in these calculations is certainly open to question. In fact Dieke and Kistiakowsky[12] from an analysis of band spectra of formaldehyde found 2.941 (10^{-40}) as the moment of inertia of the top. The value 2 (2.941)10^{-40} is larger than the one here calculated, (5.205)10^{-40}, as might be expected because of the attraction of the oxygen for the two hydrogen atoms. If one still uses 1.08A for the C−H distance, this experimental moment corresponds to an angle of 121° between the C−H bonds. But in the case of ethylene this spreading effect should be less, and hence the value 5.88 (10^{-40}) might be taken as an upper limit. In fact Badger[13] has determined the moments of inertia of ethylene from spectroscopic data, and finds for the three moments the values of 33.2, 27.5 and 5.7 (10^{-40}). These give a product of 5200 (10^{-120}), while the value actually used was 5330 (10^{-120}). This discrepancy is quite negligible.

The model of ethane is, perhaps, less doubtful; the interatomic distances are quite well established, and the tetrahedral angle must be a good approximation. The former factor should be sufficiently accurate to allow no errors greater than a few tenths of an entropy unit, and regarding the latter, elimination of the discrepancy would require the assignment of fantastic values. Were the entire fault in the moments of inertia, the product of the four principal moments (assuming classical free rotation) would have to be reduced from 34,210 (10^{-160}) to 24,660 (10^{-160}); this is obviously too radical.

Thus, although other factors may be contributory, most of the uncertainty would appear to lie in the treatment of the problem of the free rotation of the two methyl groups of ethane.

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[11] Parks and Huffman, *Free Energies of Some Organic Compounds*, Chem. Cat. Co., N. Y., 1932, p. 79.

[12] Dieke and Kistiakowsky, Phys. Rev. **45**, 4 (1934).

[13] Badger, Phys. Rev. **45**, 648 (1934).

The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites

III. The Decomposition of *n*-Propyl Nitrite

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The thermal decomposition of *n*-propyl nitrite is a homogeneous first order reaction in the temperature range 170 to 210°C. The mechanism of the decomposition is analogous to those of the other alkyl nitrites, *viz.*,

$$C_3H_7ONO \rightarrow NO + \tfrac{1}{2}C_2H_5CHO + \tfrac{1}{2}C_3H_7OH.$$

The rate of reaction is given by

$$K = 2.75 \times 10^{14} e^{-37650/RT} \text{ sec.}^{-1}.$$

The rates and activation energies of the various nitrite decompositions are compared. It is concluded that the increase in rate with the higher members of the homologous series is probably due to the participation of extra vibrational degrees of freedom. An estimate of the strength of the $-O-N-$ bond is made.

Introduction

THE investigation of the unimolecular decomposition of a series of chemically related compounds is of considerable interest. It has recently been shown in the first two papers of this series[1] that the alkyl nitrites constitute an ideal series of compounds from this point of view. Methyl and ethyl nitrites were shown to decompose homogeneously and unimolecularly. The decompositions are simple and appear to involve the simple splitting of the $-O-NO$ bond.

Since submitting this paper, our previous conclusions regarding the mechanism of the reaction have been completely confirmed by a paper by Rice and Radowskas.[2] By the free radical method they have shown that, as we suggested, the first step in the decomposition of ethyl nitrite is

$$C_2H_5NO_2 = C_2H_5O + NO.$$

Furthermore, their value of the activation energy for the split into radicals agrees with ours for the overall reaction, and hence confirms our conclusion that this split represents the rate determining step.

In consequence it is possible to make comparisons between the activation energies and reaction rates of the different members of the series. It is therefore desirable to investigate as many of the alkyl nitrites as possible. The present paper deals with the third straight chain member of the series, *viz.*, *n*-propyl nitrite.

Experimental

Reaction velocities were measured as before by observing the rate of pressure change in a system at constant volume. The reaction vessels were Pyrex bulbs having a capacity of about 125 cc. The apparatus was similar to that used previously. On account of the higher boiling point of the *n*-propyl nitrite and of some of the reaction products, it was necessary to heat the connecting tubing to a higher temperature than before. Stopcocks leading to the reaction vessel were therefore replaced by mercury seals, and the whole of the connecting tubing was heated during experiments to 105°C. Temperature measurement and control was as before. It was possible to keep the temperature constant to within 0.25°C.

Propyl nitrite was prepared in an analogous way to the previous nitrites, by the addition of a solution of nitrous acid to *n*-propyl alcohol. The liquid layer of nitrite was separated and purified by treatment with sodium carbonate solution, followed by several washings with ferrous sulphate solution to remove nitrogen oxides. It was then dried by permitting it to stand in contact with anhydrous sodium carbonate. The nitrite was then fractionally distilled and condensed twice. During the course of the investigation the *n*-propyl nitrite was stored in a cooled bulb.

[1] Steacie and Shaw, (I) Proc. Roy. Soc. **A146**, 388 (1934); (II) J. Chem. Phys. **2**, 345 (1934).
[2] Rice and Radowskas, J. Am. Chem. Soc. **56**, 214 (1935).

The Products of the Reaction

Since the form of the reaction curves and total pressure increase at completion did not vary with temperature or pressure, it follows that there cannot be much variation in the products of reaction with varying conditions.

Gas analysis was carried out on the products for nitric oxide as this was shown to be the only gaseous product when the reaction bulb was cooled down to −80°C and the gas sample pumped off for analysis. Duplicate analysis gave a value of 97 percent average for NO gas present. This result is in agreement with the overall reaction given below that is advanced for the decomposition:

$$C_3H_7ONO = NO + \tfrac{1}{2}C_3H_7OH + \tfrac{1}{2}C_2H_5CHO.$$

This equation requires that one molecule of NO be formed from one molecule of propyl nitrite. To confirm this, products were cooled to −80°C at which temperature the noncondensed NO gas registered the only pressure while the other products remained condensed. Instead of finding the NO pressure to be equivalent to that of the initial propyl nitrite, it was found to be invariably two-thirds. This low value is probably due to the formation of a complex between part of the NO and the condensed products at low temperatures. It may be stated here that a similar behavior was encountered in making runs where it was observed, with increasing initial pressure of propyl nitrite, there was a relative decrease in reaction rate. This difficulty was immediately overcome by raising the temperature of the cooler connecting tubing to 105°C when all runs at one temperature gave constant rates independent of the initial pressure, as will be shown later.

Thus it may be concluded from these facts and with a doubling of the pressure on completion of reaction that the decomposition of *n*-propyl nitrite is analogous to the previous nitrites investigated where the initial break is of the O−NO bond.

The Pressure Change Accompanying the Reaction

The mechanism given above would lead to a pressure increase of 100 percent at completion.

Table I. *Maximum pressure increases.*

Temperature (°C)	Initial pressure (cm)	Maximum pressure increase (%)
189.9	26.68	98.4
189.9	18.34	100.0
189.9	14.68	99.2
199.9	26.52	99.2
		Mean 99.2

The pressure increases obtained were almost exactly 100 percent. Some typical values are given in Table I.

We have therefore assumed that the pressure increase is a direct measure of the reaction, and that $T_{12.5}$, T_{25} and T_{50} (the times for 12.5, 25, and 50 percent pressure increase) correspond to 12.5, 25 and 50 percent reaction, respectively. On this basis the ratio T_{50}/T_{25} should be equal to 2.44 if the reaction is first order. Actually the mean value of the ratio from all runs was 2.53.

The Rate of Reaction

Complete data for two typical runs are given in Table II. The first-order constants obtained

Table II. *Data for typical runs.*

Temperature = 210°C, Initial pressure = 18.38 cm				Temperature = 190°C, Initial pressure = 14.68 cm			
Time (min.)	ΔP (cm)	% reaction	K	Time (min.)	ΔP (cm)	% reaction	K
0	0	0	—	0	0	0	—
0.5	1.50	8.2	0.172	0.5	.19	1.3	0.0257
1	2.68	14.6	0.160	1	.41	2.8	0.0272
1.5	3.54	19.3	0.145	2	.76	5.2	0.0273
2	4.33	23.6	0.136	3	1.15	7.8	0.0257
2.5	4.85	26.4	0.124	5	1.68	11.4	0.0237
3	5.36	29.1	0.119	7	2.22	15.1	0.0226
3.5	6.13	33.3	0.117	9	2.67	18.2	0.0227
4	7.11	38.6	0.124	11	3.21	21.9	0.0227
4.5	7.73	42.1	0.123	16	4.36	29.7	0.0223
5	8.28	45.1	0.122	20	5.36	36.1	0.0227
6	9.36	50.8	0.120	24	6.12	41.7	0.0228
7	10.30	56.0	0.120	32	7.53	51.2	0.0227
8	11.20	60.8	0.119	43	8.98	61.2	0.0223
9	11.96	65.0	0.118	48	9.39	64.0	0.0217
11	13.31	72.3	0.119	54	10.03	71.7	0.0216
13	14.50	78.8	0.120	60	10.53	73.8	0.0214
15	15.26	82.9	0.120	69	11.26	76.7	0.0216

are slightly high at the start, and then become very satisfactorily constant.

The summarized data for all runs are given in Table III.

The Effect of Pressure on the Rate

The constancy of the values of the fractional times with varying pressure shows that the reaction is of the first order. There is no indica-

tion of any falling off in rate at the lower pressures used. The investigation of the nitrite decompositions at low pressures is in progress and the results will be reported later.

The Effect of Surface

Experiments were made in an empty reaction vessel, and also in a vessel packed with short lengths of Pyrex tubing, so as to give an increase of about 9-fold in the surface/volume ratio. It will be seen from Table III that there was very

Table III. *The rate of reaction.*

(°C)	(cm)	$T_{12.5}$ (sec.)	T_{25} (sec.)	T_{50} (sec.)	(°C)	(cm)	$T_{12.5}$ (sec.)	T_{25} (sec.)	T_{50} (sec.)
		Empty bulb					Empty bulb		
169.9	13.77	1998	4740	—	199.9	19.24	132.0	306.0	744
180.3	11.36	864	1980	4920		26.52	148.8	326.4	756
	12.50	936	2010	4572		27.65	144.0	321.0	774
	14.78	750	1674	4572		31.24	150.0	316.2	768
	19.62	792	1644	4920		Mean	131.1	311.4	777
	Mean	836	1827	4084	209.8	18.38	51.0	136.2	348.0
189.9	14.68	335	768	1860		22.82	58.8	145.2	360.0
	17.52	366	816	2076		24.72	54.0	133.8	327.6
	18.34	285	684	1752		33.88	69.0	141.0	322.4
	21.18	320	696	1806		35.55	67.8	148.8	345.0
	21.72	306	696	1806		Mean	60.0	141.0	342.6
							Packed bulb		
	23.85	334	732	1860	189.9	9.32	265.2	666	1620
	26.68	316	678	1908		11.26	265.8	660	1620
	Mean	323.0	724	1860		18.75	319.8	774	2100
199.9	6.08	114.0	301.8	876		Mean	283.6	700	1780
	9.31	124.2	288.6	792	199.9	13.05	122.4	297.6	762
	16.49	124.2	312.6	762		14.92	121.2	301.2	738
	16.66	117.0	306.0	750		Mean	121.8	299.4	750
	17.67	125.4	324.0	774	209.8	16.70	57.6	136.8	360

little difference in rate in the two vessels. There is therefore no doubt that in the empty vessel there are no complications due to heterogeneity.

The Temperature Coefficient

In Fig. 1 the logarithms of the fractional times are plotted against $1/T$. The data used are the mean values given in Table III. From the slopes

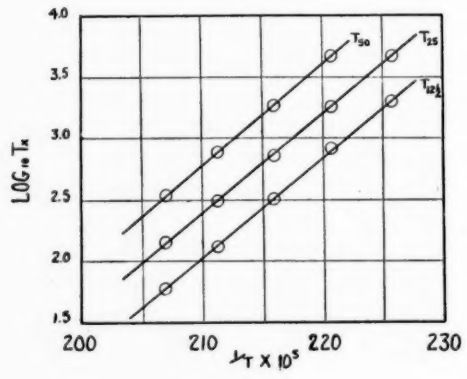

Fig. 1.

of the lines we obtain for the heat activation:

from $T_{12.5}$	37,550 calories per gram molecule
T_{25}	37,550
T_{50}	37,850
Mean	37,650

Hence the rate of reaction may be given by

$$T_{25}=1.05\times10^{-15}e^{37650/RT}\text{ sec.}$$

or, since $KT_{25}=0.288$,

$$K=2.75\times10^{14}e^{-37650/RT}\text{ sec.}^{-1}.$$

Discussion

In the past attempts have been made to compare the unimolecular decompositions of series of related compounds. In most cases, however, such attempts have not been very successful on account of complications, such as side reactions, which make the decompositions of the different members of a series not strictly comparable. In addition, in most cases previously investigated two or more chemical bonds are being broken in the overall reaction process, and this makes the actual elementary reaction very uncertain.

In the present case, there seems to be no doubt that all the nitrite decompositions so far investigated are directly comparable, and that in each case the primary reaction involves the rupture of only one chemical bond. The nitrites therefore furnish an ideal series for purposes of comparison. Obviously such a comparison can be more accurately made when measurement at low pressures have been completed, and when data are available for higher members of the series. It seems, however, to be worth while to make a qualitative comparison of the results so far obtained.

The rates of the three decompositions are given by an equation of the form

$$K=Ae^{-E/RT},\ viz:$$

Methyl Nitrite	$K=1.84\times10^{13}e^{-36400/RT}$ sec.$^{-1}$,
Ethyl Nitrite	$K=1.39\times10^{14}e^{-37700/RT}$ sec.$^{-1}$,
n-Propyl Nitrite	$K=2.75\times10^{14}e^{-37650/RT}$ sec.$^{-1}$.

The chief difficulty in making comparisons is that the exponential and nonexponential factors in the rate expression are interdependent. As a result experimental errors cause fluctuations in

the two which are much greater than the error in determining the absolute rate. It is therefore advisable perhaps, first of all to compare the velocity constants at some definite temperature. At 189.9°C we have

Methyl $K=0.97\times10^{-4}$ sec.$^{-1}$,
Ethyl $K=1.89\times10^{-4}$ sec.$^{-1}$,
Propyl $K=3.95\times10^{-4}$ sec.$^{-1}$.

Whence we have

$$K_{Me} : K_{Et} : K_{Pr}=1 : 1.95 : 4.07.$$

In other words the rate is almost exactly doubled on going from one member to the next. This is also equivalent to stating that, if we assume that the variations in E are due to experimental error, then A is approximately doubled as we go from one member of the series to the next. It seems, however, very unlikely that E should remain constant while A varies in this way, since the variation in the collision number will be comparatively small. In any case, however, there is no doubt that E changes only very slightly as we go up the series.

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The Constancy of Two Dipole Moments in the Vapor State and Their Apparent Variation in Solution

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The validity of the solution method for the determination of dipole moment is considered with particular reference to the possible variation of moment with temperature. The moments of heptyl bromide and butyl chloride in the vapor state are found to be 2.07±0.05 and 2.04±0.01, respectively, which show the absence of appreciable increase in moment in the normal alkyl chlorides and bromides with increase in the length of the carbon chain beyond ethyl. Consideration of these values together with data for the alkyl halides in solution leads to the following estimated moment values for the vapor state: *n*-propyl bromide and *n*-butyl bromide, 2.04±0.03; *n*-propyl iodide and *n*-butyl iodide, 1.93±0.04.

THESE measurements in the vapor state were made for the sake of careful comparison with previous measurements in solution upon two substances which apparently showed abnormally and improbably high values of the atomic polarization. The comparison takes on added interest now because of recent work on the effect of solvent upon the apparent value of a dipole moment determined in solution.

Because of the rise of the apparent value of the dipole moment determined in solution with rising temperature, Jenkins[1] has stated that measurements in solution cannot be used for studying the variation of the real moment with temperature. Obviously, a small variation of the apparent moment in solution with rising temperature is not to be taken as evidence of variation in the real moment of the molecule, nor has it been generally so regarded. Many apparent small rises in moment from 25° to 50° in solution[2] have not been treated as significant. An abnormally large rise, however, in the case of diethyl succinate led to further investigation[3] which established the reality of the effect along with the rise of moment with temperature in ethylene chloride and chlorobromide. At the same time, an apparent smaller rise for ethyl acetate was disregarded.

Obviously, as the real variation of moment with temperature depends upon the potential energy between the movable parts containing the dipoles, the presence of a solvent around the molecule may be expected to affect the effective value of the moment as well as its variation. Thus, the moments found for ethylene chloride,

[1] H. O. Jenkins, Trans. Faraday Soc. **30**, 739 (1934).

[2] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 527, 2115 (1931); ibid. **54**, 1854, 3230 (1932).

[3] C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr., J. Am. Chem. Soc. **53**, 4242 (1931).

chlorobromide and bromide[3, 4] in heptane solution are somewhat higher than those found for the vapors of these substances at the same temperatures[5] and show a 50 percent greater increase with temperature. The moments in benzene solution are much higher and almost independent of temperature, presumably, because of some specific effect of the solvent.[6] Ethylene chloride in solution in carbon disulfide, carbon tetrachloride and chloroform has moment values very slightly lower than in heptane[6] and with temperature coefficients like that of the vapor. Because of the tendency toward variation with temperature of apparent moment values in solution, small differences in these temperature coefficients cannot be regarded as significant. Since no relation has been found between the apparent moment of ethylene chloride in solution[6, 7] and the dielectric constant of the solvent, the moment being higher in solution than in the vapor state instead of lower as usually found, it is impossible to apply to these molecules with movable dipoles any of the empirical relations which have been developed between apparent moment and dielectric constant of the solvent. In the case of such molecules, it is obvious that the variation of polarization with temperature cannot be used to calculate the atomic polarization. Such values calculated by Smyth and Kamerling[4] for four polymethylene bromides containing two movable dipoles were enclosed in parentheses and taken as evidence of variation of the moment with temperature which made the calculated atomic polarization impossibly high. These values should not, therefore, be cited as evidence of the incorrectness of the temperature-solution method of obtaining moments.[1]

Purification of Materials

n-Heptyl bromide

Material from the Eastman Kodak Company was purified as in earlier work;[8] n_D^{20} 1.45058. Two samples were used in the dielectric constant measurements, identical results being obtained.

n-Butyl chloride

Material from the Eastman Kodak Company was refluxed gently with concentrated sulfuric acid, washed several times with water, dried over two portions of calcium chloride and distilled; b.p. 78.4–78.6°; n_D^{20} 1.40230. Repeated treatment did not change the refractive index.

Experimental Results

The dielectric constants ϵ were determined with the apparatus previously described,[9] heptyl bromide being measured in a copper cell and butyl chloride in a gold-palladium cell. The polarization P was calculated by means of the equation $P=[(\epsilon-1)/(\epsilon+2)]V$, in which V is the molar volume. For heptyl bromide, the polarization at each temperature was taken as the average of from three to eight measurements at pressures between 35 and 162 mm, the error caused by deviation from the ideal gas laws at these pressures being small. For butyl chloride, five to eight determinations at each temperature were made over a range of pressure extending to higher values and extrapolated to zero pressure to obtain a value P_0 which should be free from error due to gas law deviations. For heptyl bromide the temperature range of the measurements was so limited by the tendency toward thermal decomposition at higher temperatures that the dipole moment μ was calculated at each temperature by means of the equation $\mu=0.01273[(P-MR_D)T]^{\frac{1}{2}}$, in which MR_D is the molar refraction for the D sodium line. The more accurate equation $P=a+b/T$ was applied to the butyl chloride results and the moment was calculated as $\mu=0.01273\times10^{-18}b^{\frac{1}{2}}$, while the atomic polarization was obtained as $P_A=a-P_E$, the difference between a, the total induced polarization, and P_E, the molar refraction extrapolated to infinite wavelength.

Discussion of Results

The two values previously found for the moment of heptyl bromide, 1.83 in heptane

[4] C. P. Smyth and S. E. Kamerling, J. Am. Chem. Soc. **53**, 2988 (1931).
[5] C. T. Zahn, Phys. Rev. **38**, 521 (1931); ibid. **40**, 291 (1932).
[6] A. E. Stearn and C. P. Smyth, J. Am. Chem. Soc. **56**, 1667 (1934).
[7] H. Müller, Physik. Zeits. **34**, 689 (1933).
[8] C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. **52**, 2227 (1930).
[9] K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. **55**, 453 (1933).

solution[8] and 1.85 in benzene solution,[10] were in excellent agreement, but the value obtained in heptane solution was calculated from the variation of the polarization with temperature. This method gave the high value 15.5 for the atomic polarization, values of this magnitude having since been shown to be incorrect,[11] and a correspondingly low value for the moment. When the moment is calculated from the value obtained by Smyth and Rogers for the polarization at each temperature by means of the equation $\mu=0.01273[(P_\infty-MR_D)T]^{\frac{1}{2}}$, the values rise from 1.97 at 223°K to 2.02 at 303°K. One may apply to these data the empirical equation of Müller,[7] $P_{M\text{gas}}=P_{M\text{sol}}/[1-0.075(\epsilon-1)^2]$, where $P_M=P_\infty-MR_D$ and ϵ is the dielectric constant of the solvent. The moment values obtained from these values of P_M calculated for the gaseous condition increase from 2.05 at 223°K to 2.09 at 303°K. If 3.5 is added to the value 42.3 used for MR_D in order to account for the atomic polarization, the moment calculated for the gas from the liquid measurements increases from 2.02 to 2.04 over this range of temperature. The use of this value $P_E+P_A=45.8$ to calculate the moment from the gas measurements gives a mean value 2.09. Since this is higher than the mean value 2.03 calculated in the same way from the empirically corrected solution values and since such deviations from the gas laws as may have occurred would tend to make the polarization and, hence, the moment values high, it seems reasonable to assign a value 2.07 ± 0.05 to the moment of heptyl bromide. The difference between this value and the accurate value 2.02 found for ethyl bromide vapor[12] is equal to the probable error in the determination.

The accurate values for butyl chloride in Table I show, as in the case of heptyl bromide, that the atomic polarization value 13.6 obtained from the variation of polarization in heptane solution with temperature[8] was high and the moment value 1.88 correspondingly low. Calculation of the moment from these solution polarizations by subtraction of the molar refraction gives values rising from 1.98 at 183°K to 2.07 at 343°K. These values are close to those found by Parts,[13] 1.97 at 283°K in benzene solution and the approximate value 2.00 calculated from a variation of polarization with temperature over a range of only 40°. Calculation of the polarizations in heptane to the vapor state by means of the Müller equation leads to moment values rising from 2.07 at 183°K to 2.13 at 343°K. If, however, the polarization values thus calculated to the vapor state are diminished by 3.0, the difference between the value of a in Table I and MR_D, the moment variation is reduced to a rise from 2.05 to 2.09 over this temperature range. These values are close to the accurate value 2.04 in Table I.

TABLE I. *Polarizations and dipole moments.*

n-Heptyl bromide			*n-Butyl chloride*	
T, °K	P	$\mu\times10^{18}$	T, °K	P_0
372.8	117.7	2.13	314.7	109.9
373.5	120.3	2.17	337.4	104.5
377.0	116.3	2.13	379.1	96.4
388.5	114.9	2.14	405.5	91.7
393.0	113.3	2.13	428.2	88.1_5
395.5	115.5	2.17	479.6	82.0_5
414.8	112.0	2.16	$a=28.5$, $P_A=3.6$, $\mu=2.04\times10^{-18}$	
415.8	111.2	2.15		
423.3	110.0	2.16		
433.8	108.2	2.15		
Mean value = 2.15				

The identity of the moment of *n*-butyl chloride with the accurate value 2.04 found by Sänger[14] for *n*-propyl chloride and the closeness of both values to the most accurate found for ethyl chloride, 2.05 by Fuchs[15] and 2.02 by Sänger shows the absence of detectable increase in moment with increase in the length of the chain of the alkyl chloride beyond two carbons. The variation with temperature of the polarization of butyl bromide in solution in heptane[8] gave a high atomic polarization 19.3 and a low moment 1.81. Calculation of the moment by subtracting the molecular refraction MR_D gives 1.97 at 183°K, identical with the value found by Parts at 283°K in benzene solution, and 2.08 at 343°K. Subtraction of an additional 3.5 to take care approximately of the atomic polarization and application of the Müller equation to these data

[10] J. Errera and M. L. Sherrill, J. Am. Chem. Soc. **52**, 1993 (1930).
[11] C. P. Smyth, J. Chem. Phys. **1**, 247 (1933).
[12] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **2**, 499 (1934).
[13] A. Parts, Zeits. f. physik. Chemie **B7**, 327 (1930).
[14] R. Sänger, Helv. Phys. Acta **3**, 161 (1930); Physik. Zeits. **32**, 20 (1931).
[15] O. Fuchs, Zeits. f. Physik **63**, 824 (1930).

give 2.02 at 183°K and 2.09 at 343°K. The mean of these two values 2.06 is indistinguishable from the mean 2.07 found in similar fashion for butyl chloride. With the moment of ethyl bromide vapor 2.02,[12] it is probable that the moments of propyl and butyl bromide vapors differ by no more than 0.03 from 2.04, which differs by no more than the probable error from the value 2.07 here determined for heptyl bromide. The variation with temperature of the polarization of butyl iodide in solution[8] gave a very high atomic polarization 21.9 and a correspondingly low moment value 1.59. Calculation of the moment from these data by use of the molecular refraction gives values rising from 1.80 at 193°K to 1.87 at 293°K. In view of the accurate value 1.90 for the moment of ethyl iodide vapor,[12] it is probable that the moments of *n*-propyl and of *n*-butyl iodide vapor differ from 1.93 by no more than 0.04.

It is evident from these calculations of apparent moment values at different temperatures in solution as well as from a tendency toward increase between values at 25° and 50° previously published[2] that, in many cases, the apparent value of the moment in solution increases with rising temperature. The change of polarization with temperature thus involved affects the slope of the $P-1/T$ curve so as to give too large a value of a and a correspondingly small value of b. Although the method of plotting polarizations in solution against $1/T$ has given satisfactory values for the moments in solution of chlorobenzene, chloroform[16] and *tert.*-butyl chloride,[17] it is evidently wholly unsatisfactory for the *n*-alkyl halides and cannot, therefore, be generally employed with safety.

In view of the dependence of the apparent polarization and moment of the solute upon the dielectric constant of the solvent found by Müller,[7, 18] it follows that the apparent value of a moment in solution should rise as the dielectric constant of the solvent decreases with rising temperature. Jenkins[1] has been able to account for increase in the apparent moment of nitrobenzene in solution in dekalin with rising temperature entirely by the effect of the decrease in the dielectric constant of the dekalin. However, the results of the calculations given in this paper show that in the case of heptyl bromide and butyl chloride, the effect of change in the dielectric constant of the solvent as calculated directly by Müller's equation accounts for only about one-third of the apparent variation. When allowance is made also for atomic polarization, the apparent variation is reduced to about one-half. The qualitative explanation previously given[11] for the incorrectness of the abnormally high atomic polarization values involves much the same fundamental idea as do these empirical equations for the effect of solvent. It may be said that the apparent moment found for a molecule in solution is influenced by the internal field acting on the molecule. Although the effect of this internal field, which decreases with rising temperature, is greatly reduced by extrapolation to infinite dilution and, sometimes, wholly eliminated by the further use of an empirical equation involving the dielectric constant of the solvent, a small error may yet remain in the moment values obtained from solution. As a matter of fact, this was shown by Müller's discovery that there were other substances in addition to those containing movable dipoles to which his equation did not apply. The failure to eliminate entirely this effect of the internal field may evidently have only a small influence upon the moment value determined at one temperature, but may seriously impair the accuracy of values determined from the variation of polarization with temperature.

[16] C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc. **50**, 1547 (1928).

[17] C. P. Smyth and R. W. Dornte, J. Am. Chem. Soc. **53**, 545 (1931).

[18] See also, H. O. Jenkins, Nature **133**, 106 (1934) and S. Sugden, ibid. **133**, 415 (1934).

The Atomic Distribution in Red and Black Phosphorus and the Crystal Structure of Black Phosphorus

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No satisfactory crystal structure determination has been made of any of the forms of phosphorus. Five samples of black phosphorus gave identical powder patterns different from those reported by Linck and Jung, whose rhombohedral structure gives improbable interatomic distances and coordination. A sample which had been prepared at room temperature and 35,000 atmospheres gave the diffuse rings of an "amorphous" x-ray pattern. Another sample, prepared at 300°C and 8000 atmospheres, is a new form of phosphorus, having the same density as black. Atomic distribution curves of crystalline and "amorphous" black and red phosphorus were obtained by the method of Fourier analysis. All four gave practically the same curve, showing three neighbors at 2.28A and about twelve at 3.6A. With the aid of the atomic distribution curves and the fact that certain lines showed a preferred orientation, it was possible to determine the structure of black phosphorus. It consists of double layers; the cell is side-centered orthorhombic with $a=3.31$A, $b=4.38$A and $c=10.50$A. There are eight atoms in the cell, giving a calculated density of 2.69 compared with 2.70 observed. The space group is $V_h^{18}-Bmab$. The black phosphorus structure allows a closer packing than the arsenic structure, where the atomic environment is similar, and so is favored by the high pressure.

INTRODUCTION

PHOSPHORUS crystallizes in a number of allotropic forms, three of which are easily distinguished because of their widely differing physical and chemical properties. These three forms are the red, white and black varieties. Their peculiar conditions of formation and transformation make their study of interest in the theory of the dynamics of crystalline changes. The data on phosphorus are confusing and incomplete.[1] None of the crystal structures have been satisfactorily worked out by x-ray methods; the various investigators do not even agree on the positions of the lines in the powder patterns.

PROPERTIES OF THE ALLOTROPIC FORMS OF PHOSPHORUS

When heated, all three forms sublime to a vapor composed of P_4 molecules, which yields white phosphorus when condensed. However, at lower temperatures (100°C in a vacuum), the vapor of red phosphorus condenses to give red phosphorus; but the vapor density is so low that no molecular weight determination has been made. White phosphorus is easily changed to red by the action of heat, light or x-rays. Under a pressure of 12,000 atmospheres and at a temperature of 200°C, it changes to black phosphorus.[2] Red phosphorus does not change under these conditions.† Black phosphorus changes to red when heated to 550°C. All of these changes are irreversible.

The physical differences between these forms are striking as shown in Table I.

TABLE I. *Physical properties of the forms of phosphorus.*

COLOR	DENSITY	M.P.	B.P.	INFLAMMABILITY	SOLUBILITY
White	1.83	44.1	280	Very high	Soluble in number of organic solvents with mol. wt. P_4
Red	2.34	590	725	High	Insoluble
Black	2.70	—	—	Low	Insoluble

These facts seem to indicate that white phosphorus is composed of more or less loosely bound P_4 molecules which readily break up to form the more stable structures of red and black phosphorus, which consist of larger molecules or else are continuous, nonmolecular structures.

White phosphorus can be obtained in beautiful, transparent crystals of the cubic system by crystallization from solution or by slow sublima-

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[1] For a discussion of physical and chemical properties of phosphorus see Ephraim. *Anorganische Chemie*, Steinkopff, Dresden and Leipzig, 1934, pp. 87–92.

[2] P. W. Bridgman, J. Am. Chem. Soc. **36**, 1344 (1914).

† Professor Bridgman has recently succeeded in changing red phosphorus to black by the application of a shearing stress at very high pressures.

tion. Jung[3] reports that x-ray analysis is impossible since the x-rays transform the white to the red form. However, Natta and Passerini[4] announced that by cooling the sample to $-35°C$ and by using iron radiation, they were able to obtain 22 lines of a cubic pattern with $a=7.17$A. But they failed to publish their data or the crystal structure.

Red phosphorus in its commercial form gives diffuse rings in its x-ray pattern and is supposed to be amorphous. After suitable heat treatment it gives a normal line pattern. Red phosphorus is usually considered to be either a finely divided form of violet phosphorus or a solution of white in violet because of similarity in physical properties. Frost,[5] however, has shown by x-ray evidence that they have different crystalline forms. He concluded from his powder patterns that both structures had a low symmetry. *Violet phosphorus* can be obtained in small, transparent, monoclinic crystals by crystallization from molten lead. Olshausen[6] and Jung[3] report patterns which do not agree with either of the patterns of Frost, nor do they agree with one another. Olshausen used red phosphorus and Jung, violet.

Black phosphorus resembles graphite when pulverized. Linck and Jung[7] assign it a rhombohedral cell on the basis of their x-ray pictures. However, the coordination of atoms in their cell (one nearest neighbor at 2.46A and six at 3.01A) does not agree with the accepted atomic radius of 1.10A, nor does it give the three or five nearest neighbors to be expected from a covalent structure.

Experimental Work

We were fortunate in securing seven samples of black phosphorus from Professor Bridgman at Harvard. Five of these were prepared at the usual temperature of 200°C and pressures of 12,000 atmospheres or more. These samples varied in age from a few months to twenty years. All gave identical powder patterns which were not the same as those reported by Linck and Jung.[7] Heat treatments of 100 hours at 450°C and two hours at 550°C failed to change the patterns in any way except to make the lines somewhat sharper. Linck and Jung had used samples from the same source and the physical properties they describe are the same as those we observed. We are at a loss to account for the discrepancy in the patterns.

The other two samples had been made under different conditions. One was made at room temperature and 35,000 atmospheres.[8] Its physical properties were similar to those of the other samples except that it had a density of 2.6 instead of 2.7. Its powder pattern showed diffuse rings instead of sharp lines. The other had been made by Dr. F. Birch at 300°C and 8000 atmospheres and gave a powder entirely different in appearance from the other samples. It had a deep red color and no flakiness. Its x-ray pattern was different from any of the other forms of phosphorus. It is a new form of phosphorus which we have not found time to investigate further.

Samples of commercial, "amorphous" red phosphorus were obtained from the stock room and showed diffuse rings on the powder pattern. We also obtained a sample of red phosphorus from Professor Bridgman which had withstood a pressure of 12,000 atmospheres without change, and prepared other samples by heating black phosphorus to 550°C in a sealed quartz tube. All of the samples except, of course, commercial red phosphorus, gave the same set of x-ray lines which checked that of Frost[5] for red phosphorus.

We have applied the method of Fourier analysis to the x-ray powder patterns of black and red phosphorus. This method, which was developed by Zernike and Prins[9] and by Debye and Menke,[10] yields information about the distances between atoms, but nothing about their arrangement in the crystalline lattice. It has been used as an aid in crystal structure determinations by Warren and Gingrich[11] and by Warren.[12]

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[3] Jung, Centralblatt f. Min. u. Geol. 1926, 107–114.
[4] Natta and Passerini, Nature **125**, 707 (1930).
[5] Frost, J. Russ. Phys. Chem. Soc. **62**, 2235 (1930).
[6] Olshausen, Zeits. f. Krist. **61**, 463 (1925).
[7] Linck and Jung, Zeits. f. anorg. Chemie **147**, 288 (1925).
[8] P. W. Bridgman, Phys. Rev. **45**, 844 (1934).
[9] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).
[10] Debye and Menke, Erg. d. Techn. Röntgenkunde II.
[11] Warren and Gingrich, Phys. Rev. **46**, 368 (1934).
[12] Warren, J. Chem. Phys. **2**, 551 (1934).

Atomic Distribution Curves

Assuming that each phosphorus atom has the same environment, the density of atoms at a distance r from a given atom can be obtained from the following formula:[11]

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+(2r/\pi)\int_0^\infty si(s)\sin(rs)ds,$$

where $s=4\pi\sin\theta/\lambda$,
ρ_0 = average density of sample in atoms per unit volume,
$\rho(r)$ = average density of atoms at a distance r from a given atom,
$i(s)=(I/N-f^2)/f^2$,
I = experimental intensity corrected for absorption, incoherent radiation and polarization, including polarization due to the monochromatizing crystal,
f^2 = intensity of independent scattering per atom,
N = number of scattering atoms.

Consequently $4\pi r^2\rho(r)dr$ represents the number of atoms between r and $r+dr$.

The analysis was carried out in the usual way[11, 12] except for the determination of the constant N, which was evaluated from the following formula:*

$$N=\int_0^{10}Isds/\int_0^{10}f^2sds.$$

Molybdenum $K\alpha$ radiation was used, monochromatized by a sodium chloride crystal. The camera had a radius of 47 mm and the exposures

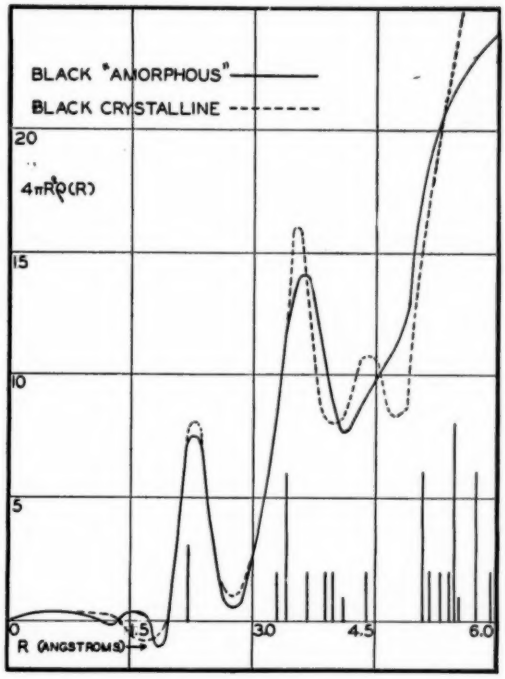

FIG. 1. Atomic distribution in black phosphorus. The solid vertical lines indicate the distribution in the crystal structure found for black phosphorus.

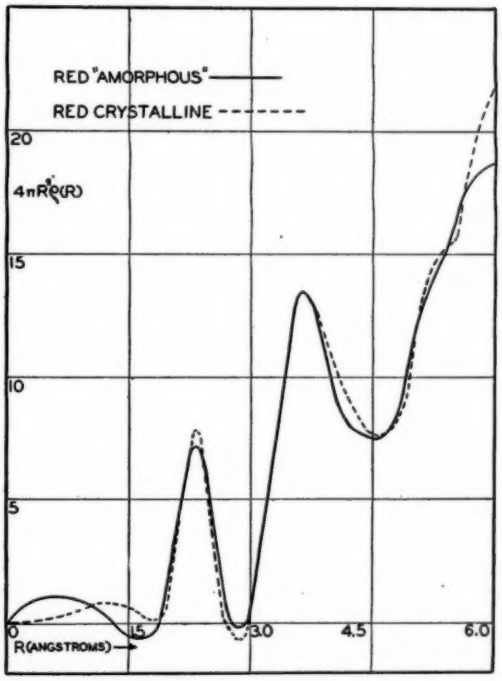

FIG. 2. Atomic distribution in red phosphorus.

* At large angles the experimental error in the determination of intensity is high, partly due to the small intensities involved and partly due to the large uncertain correction for incoherent intensity. Hence the assumption that $I=Nf^2$ at some arbitrary large angle may give a result which is far from correct. A better way is to choose N so that the deviations of the experimental curve from independent scattering more or less balance one another at large angles. A method which depends only a little on the inaccurate measurements at large angles is the following. From the formula:[11]

$$I=Nf^2\{1+\int_0^\infty 4\pi r^2[\rho(r)-\rho_0](\sin(sr)/sr)dr\}$$

we easily obtain

$$\int_0^S Isds-N\int_0^S f^2sds$$
$$=4\pi N\int_0^\infty\int_0^S f^2\sin(sr)r[\rho(r)-\rho_0]dsdr=K.$$

It can be shown that if S is chosen large enough, the value of K is small compared with that of the other two integrals, so it is justifiable to assume K to be zero as a first approximation. We found after doing this that its actual value was about eight percent of the other integrals, hence a second approximation was unnecessary. The error in the first approximation can be estimated in advance by integrating K over the region where $\rho(r)$ is known to be zero. In the case of phosphorus this estimate was 11 percent.

required several days. It was found that errors due to stray radiation or to incorrect determination of N had a considerable effect on the values of density determined, but that the positions of the peaks remained remarkably constant.

The results of the analysis are shown in Figs. 1 and 2. The four samples analyzed; crystalline and "amorphous" black phosphorus and crystalline and commercial red phosphorus gave nearly the same distribution curves. The supposedly amorphous samples each show four bands at the positions where the crystalline samples have their strongest lines. Probably they are simply extremely fine crystals. The area under the first peak is 3.3, indicating three neighbors at about 2.28A. The second peak is at 3.6A and has an area indicating about twelve atoms at that distance. The red phosphorus distribution curves show peaks slightly farther out than those of black.

The Crystal Structure of Black Phosphorus

The interplanar spacings of black phosphorus were accurately determined from powder patterns made with filtered iron radiation from a Hadding tube. In one case iron and in another sodium chloride was mixed with the sample as a standardizing substance. The results usually varied from one another less than 0.005A. Supplementary photographs from a copper tube checked the intensities and approximate positions of the lines, and also yielded a few more faint lines. The camera used had a radius of 47 mm.

The interplanar spacings found will not fit a cubic, tetragonal or hexagonal lattice. Ordinarily, it is hopeless to try to solve a structure of lower symmetry from powder photographs alone. Fortunately, the results of the Fourier analysis, together with the fact that one of the lines and its two higher orders showed preferred orientation, made it possible to determine the structure. The physical properties of the powder and the preferred orientation of the lines indicated a layer structure with the layers 5.25A apart.

The second order of the line showing preferred orientation is stronger than the first, while the third is weaker. A rough calculation shows that each layer must be double with a spacing of about 2.1A between halves. In satisfying this condition and the distribution determined from the Fourier analysis, we are led to an orthorhombic cell of which we know the approximate dimensions. Trial shows that the c axis must be double the layer spacing and more accurate values for the a and b axes are determined from the first few lines. It soon becomes evident that the true lattice is side-centered orthorhombic with the following dimensions:

$$a=3.31\text{A};\ b=4.38\text{A};\ c=10.50\text{A}.$$

The unit cell contains eight atoms, which gives a calculated density of 2.69, compared with the observed value, 2.70. The space group is

$$V_h^{18}-Bmab$$

with the eight atoms in the following positions:

$$0uv;\ \tfrac{1}{2},\ \tfrac{1}{2}-u,\ v;\ \tfrac{1}{2},\ u,\ \tfrac{1}{2}+v;\ 0,\ \tfrac{1}{2}-u,\ \tfrac{1}{2}+v;$$
$$0\bar{u}\bar{v};\ \tfrac{1}{2},\ \tfrac{1}{2}+u,\ \bar{v};\ \tfrac{1}{2},\ \bar{u},\ \tfrac{1}{2}-v;\ 0,\ \tfrac{1}{2}+u,\ \tfrac{1}{2}-v.$$

The best agreement of intensities is obtained for $u=0.090$ and $v=0.098$.

Calculated and observed interplanar spacings and intensities of the first 42 possible lines of this space group are shown in Table II. The agreement is excellent in nearly all cases. The few small deviations are due to preferred orientation, which cannot always be allowed for, tending to make planes near (00l) stronger and other planes weaker. Allowance for the temperature factor would make the calculated intensity for planes of smaller d, smaller. After the unit cell is once

Table II. *Calculated and observed interplanar spacings and intensities for black phosphorus.*

hkl	$d_{calc.}$	$d_{obs.}$	$I_{calc.}$	$I_{obs.}$	*hkl*	$d_{calc.}$	$d_{obs.}$	$I_{calc.}$	$I_{obs.}$
002	5.25	5.24	180	3	214	1.334	1.33*	53	½
012	3.36	3.36	396	7	131	1.325	—	5	0
004	2.62	2.62	283	5	220	1.320	—	42	0
111	2.56	2.56	837	9	008	1.313	—	5	0
014	2.25	2.25	75	1½	117	1.304	1.30*	52	½
020	2.19	2.19	57	1	222	1.280	—	10	0
113	2.11	2.11	60	1	034	1.276	1.27*	89	½
022	2.02	—	10	0	018	1.257	1.249	64	1
121	1.80	1.80	214	2	133	1.248	—	0	0
006	1.75	1.75	136	1½	206	1.203	1.200	176	2
024	1.68	—	37	0	224	1.180	1.18*	54	½
200	1.655	1.640	165	7	216	1.160	1.156	40	4
115	1.644		460		127	1.159		354	
016	1.625	—	25	0	135	1.127	—	8	0
123	1.619	1.618	472	6	028	1.126	—	2	0
202	1.579	—	33	0	036	1.121	—	75	0
212	1.485	1.483	137	2	040	1.095	—	63	0
032	1.407	1.400	218	4	232	1.072	1.067	580	4
204	1.400		149		042	1.072		15	
125	1.378	—	1	0	119	1.067	1.062	264	5
026	1.367	1.364	32	½	311	1.065		320	

* Measured with less accuracy from copper radiation.

discovered, the determination is rigorous. The atomic distribution is shown in Fig. 1 for the crystal as well as that determined by Fourier analysis. The agreement is very good, except that the Fourier analysis gives slightly too large distances.

Discussion of Results

The unit cell of black phosphorus consists of two double layers, one of which is shown in Fig. 3. Each atom is bonded to three nearest neighbors at 2.18A, in agreement with the accepted atomic radius of 1.10A, and with the coordination to be expected from covalent bonding of phosphorus. Two of the bonds are in the plane of the layer, at 99° from one another; the third is between layer halves at 103° 30′ from both, making the average bond angle 102°. This agrees with the tendency of bond angles to be nearer tetrahedral for the lighter elements of the periodic group. Thus for the fifth period the trend is: P 102°, As 97°, Sb 96° and Bi 94°. The atomic environment is quite similar to that in the arsenic structure, which is assumed by the other members of the group, except nitrogen. The difference consists in the fact that in the latter structure all bonds are between halves of the double layer, while in the former only one-third of the bonds are.

The question arises as to why phosphorus does not assume the arsenic structure. A good reason is that the black phosphorus structure is closer packed than the arsenic structure and so is favored by the high pressure under which black phosphorus is formed. If phosphorus assumed the arsenic structure, retaining the bond distances and angles of black phosphorus and also the closest distance of approach between atoms in different layers, it would have a density of only 2.44 instead of 2.69. Arsenic at high pressures might be expected to take the black phosphorus structure since, by doing so, its density would be increased from 5.73 to 6.43.

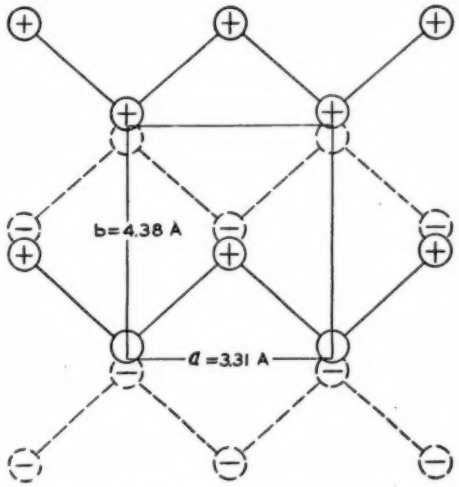

Fig. 3. A double layer of the black phosphorus structure. "+" and "−" indicate that the atom is, respectively, 0.098 c above or 0.098 c below the plane of the paper.

The fact that it has not been observed is not a conclusive argument against its possibility, since, as we saw, black phosphorus forms only under special conditions.

In this connection it should be pointed out that arsenic is a good deal more metallic than black phosphorus, having a specific resistance of 35×10^{-6} ohm cm compared with 0.711 ohm cm for the latter.[2] The decisively covalent character of phosphorus is nicely shown by the fact that the distance between bonded atoms is only 2.18A compared with 3.68A as the closest approach between atoms in different layers. In arsenic the bonds are less sharply differentiated; three nearest neighbors are at 2.51A, with three more atoms at 3.15A.

The Fourier analysis furnishes a valuable clue to the structure of red phosphorus. We know that each atom forms three covalent bonds in the normal manner. The fact that the second peak is at practically the same position as in black phosphorus suggests that the bond angles are nearly the same.

The Number of Canonical Structures of Each Degree of Excitation for an Unsaturated or Aromatic Hydrocarbon

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A simple procedure is outlined for obtaining the number of canonical structures of each degree of excitation for an arbitrary hydrocarbon molecule. The results are applied to the approximate calculation of the energies of a number of such systems.

IN the quantum-mechanical treatment of the unsaturated and aromatic hydrocarbons, and of the free radicals,[1] it is frequently desirable to know the number of canonical structures of each degree of excitation.[2] These figures can be obtained, of course, by writing down all the structures, and by then determining the number of each type by actual count. This becomes quite impracticable, however, with complicated molecules,[3] and some simpler procedure is necessary.

DESCRIPTION OF THE METHOD

The orbitals are first arranged formally in a circle in the usual manner.[4] There is some arbitrariness in this step, since in general the final result will depend upon the way in which the initial ordering is carried out. Thus, if the six orbitals in benzene are arranged in the sequence 1, 2, 3, 4, 5, 6, in which they come in the molecule itself, there are 2 unexcited and 3 first excited structures. On the other hand, if they are arranged in the sequence 1, 3, 5, 2, 4, 6, there are 0 unexcited, 1 first excited, 3 second excited, and 1 third excited structures. This causes no great difficulty, however, since there is usually one single order which is more logical than any of the others (for benzene, for example, the first of the two given above), and, in any case, the problem is uniquely determined when once the order has been established.

The general procedure will be to associate with each molecule, or grouping of atoms, a polynomial of the form

$$k_0+k_1z+k_2z^2+k_3z^3+\cdots+k_nz^n,$$

where k_i is the number of structures of the ith degree of excitation, and z is simply a parameter. Obviously, finding the polynomial which corresponds to a given molecule is completely equivalent to solving the problem as originally formulated, since the coefficients k_i are themselves the desired quantities.

I. THE MOLECULE CONSISTS OF A STRAIGHT CHAIN

The orbitals are arranged in the circle in the same order in which they come in the chain. The polynomial C_N, associated with the chain of $2N$ atoms, is given by the recursion formula

$$C_N=C_{N-1}+z\sum_{j=2}^{N}C_{j-1}C_{N-j},$$

which is derived in the following manner:

[1] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933). L. Pauling and J. Sherman, ibid. **1**, 679 (1933). G. W. Wheland, ibid. **2**, 474 (1934); **3**, 230 (1935).

[2] The significance of the terms used here is as follows (cf. reference 1): In the method which is used by Pauling and his co-workers, and to which the conclusions reached in this paper are applicable, only the interactions between the $[p]_A$ orbitals are considered. These latter are arranged formally in a circle or polygon, and all structures are drawn in which each bond lies wholly within the figure, and in which no two bonds intersect. The structures thus obtained form the "canonical" set, and are the only ones which need be considered (cf. reference 4). The various bonds are of two types: "effective" bonds between orbitals that are actually adjacent in the molecule, and "ineffective" bonds between orbitals that are not adjacent. To the degree of approximation of the present treatment, the latter do not contribute to the stability of the molecule and are introduced solely in consequence of the mathematical formalism of the method. A structure in which all bonds are effective is called "unexcited"; a structure in which one bond is ineffective is called "first excited," and so on.

[3] This is seen from the fact that the number of canonical structures for a system of $2N$ orbitals, each occupied by a single electron, is given by the expression $(2N)!/N!(N+1)!$, which increases very rapidly with N. Thus, with $2N=14$, there are already 429 structures.

[4] G. Rumer, Nachr. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse, p. 337, 1932. L. Pauling, J. Chem. Phys. **1**, 280 (1933).

We first number the orbitals in order, from 1 at one end of the chain to $2N$ at the other end. Now we consider the canonical structures which contain a bond between orbital 1 and some other definite orbital, say $2j$. This bond divides the molecule into three parts: (1) the orbitals 1 and $2j$ involved in the bond; (2) the orbitals 2, 3, $\cdots$ $2j-1$ lying on one side of the bond; and (3) the orbitals $2j+1$, $2j+2$, $\cdots$ $2N$ lying on the other side of the bond. (In the special cases in which $j=1$, or N, the second, or the third, part will be missing. We then simply treat the missing part formally as a chain of 0 orbitals, and associate with it the polynomial $C_0=1$.) If these three parts are considered separately, they can be represented by the polynomials J_1, J_2 and J_3, respectively. Then $J_1=1$ if $j=1$ (i.e., if the bond between orbitals 1 and $2j$ is effective) and $J_1=z$ otherwise (i.e., if the bond is ineffective). Similarly $J_2=C_{j-1}$, and $J_3=C_{N-j}$. If the three parts are now considered as a whole, the corresponding polynomial, which represents the totality of structures with a bond between orbitals 1 and $2j$, is the product $J_1J_2J_3$. This follows from the fact that there can be no bonds between any two of the three parts, since such bonds would necessarily lead to noncanonical structures. The law for combining such noninteracting systems is then formally identical with that for multiplying polynomials. We now consider the canonical structures in which the orbital 1 is bonded with some further definite orbital, say $2k$. As in the previous case, the associated polynomial is equal to $K_1K_2K_3$, with $K_1=1$ or z, $K_2=C_{k-1}$, and $K_3=C_{N-k}$. Obviously none of the structures of this second group will occur also in the first group, and consequently the totality of structures in which the orbital 1 is bonded to either $2j$ or $2k$ will be represented by the sum $J_1J_2J_3+K_1K_2K_3$. This same procedure can now be repeated until all of the possible canonical structures have been taken into consideration. The resulting polynomial is then

$$C_N=\sum_{j=1}^{N} J_1J_2J_3,$$

which is just the recursion formula given originally.

Since we have adopted the convention that $C_0=1$, and since we see at once that $C_1=1$, we can find the remaining polynomials in order. The first few members of the series are:

$$\begin{aligned}
C_1&=1,\\
C_2&=1+z,\\
C_3&=1+3z+z^2,\\
C_4&=1+6z+6z^2+z^3,\\
C_5&=1+10z+20z^2+10z^3+z^4.
\end{aligned}$$

In general:

$$C_N=\sum_{j=0}^{N-1}\frac{N!(N-1)!}{j!(j+1)!(N-j)!(N-j-1)!}z^j$$

$$=\frac{1}{N}\sum_{j=0}^{N-1}\binom{N}{j}\binom{N}{j+1}z^j.$$

II. The Molecule Consists of a Ring

For a ring of $2N$ orbitals, we can carry through the same sort of procedure as in the case of the chain. The result is then

$$R_N=2C_{N-1}+z\sum_{j=2}^{N-1}C_{j-1}C_{N-j}.$$

This can be expressed more conveniently as

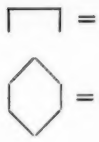
$$R_N=C_N+(1-z)C_{N-1},$$

in which form it is seen to be a special case of the general rule given below in III. The first few members of the series are:

$$\begin{aligned}
R_2&=2,\\
R_3&=2+3z,\\
R_4&=2+8z+4z^2,\\
R_5&=2+15z+20z^2+5z^3.
\end{aligned}$$

III. The Molecule Contains Several Rings

It is convenient to represent the polynomial associated with a given molecule by means of a geometrical figure, which is constructed in the following way: After the orbitals are arranged in the circle, or polygon, lines are drawn connecting each pair of orbitals which are adjacent in the actual molecule, that is, each pair of orbitals for which the corresponding exchange integral is to be set equal to α. Thus we have, for example:

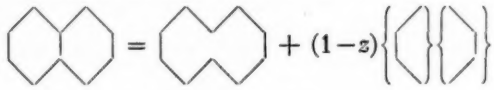


$= C_2 = 1 + z,$

$= R_3 = 2 + 3z,$

and so on.

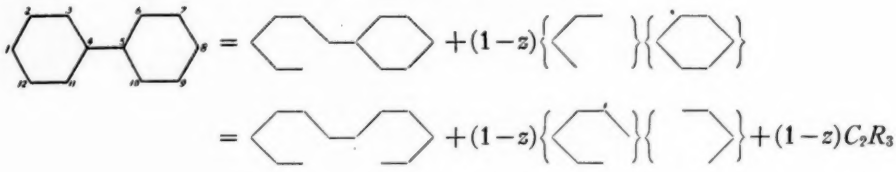
Now let us consider the relation between two figures which differ only in that one contains a single line which is absent from the other, as for example: , corresponding to naphthalene, and , corresponding to cyclodecapentane. For such cases, there is a general rule: If a figure, A, differs from a second, B, by having a single additional line, and if this line, together with its end points, divides A into two parts, C and D, then $A=B+(1-z)CD$. The derivation of this equation follows from the same considerations as were used in I. Thus we consider the totality of the structures of each molecule in which there is a bond along this added line. In A these are represented by the product CD, and in B by the product zCD. Structures which do not contain this bond are not affected in degree of excitation by the added line. This completes the proof. The theorem, when applied to naphthalene, gives



$$=R_5+(1-z)C_2^2$$
$$=3+16z+19z^2+4z^3.$$

We find, then, that naphthalene has 3 unexcited, 16 first excited, 19 second excited, and 4 third excited structures, in agreement with the direct evaluation by Pauling and Wheland.[1]

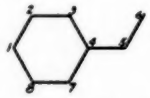
A slightly more complicated example is afforded by biphenyl.[5]



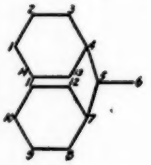
$$=C_6+(1-z)C_3C_2+(1-z)C_2R_3$$
$$=4+21z+48z^2+44z^3+14z^4+z^5.$$

This result has been checked by writing down all 132 canonical structures, and counting the number of each degree of excitation.

A few further examples are given below:

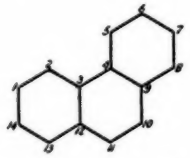
Phenylethylene  $=2+6z+5z^2+z^3,$

Sym. diphenylethylene $=4+33z+113z^2+165z^3+94z^4+19z^5+z^6,$

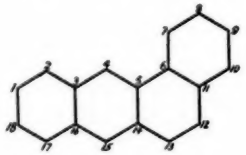
Unsym. diphenylethylene  $=4+24z+95z^2+132z^3+134z^4+33z^5+7z^6,$

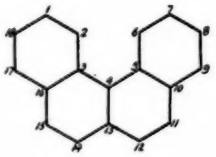
[5] Here, and in the following, we do not arrange the orbitals actually in a circle or polygon, but in whatever type of figure is most convenient for the purpose at hand. In cases in which there may be some question, the orbitals will be numbered, to indicate the sequence which they would follow if they had been arranged in the polygon. It is absolutely essential that the same sequence be maintained throughout a given calculation.

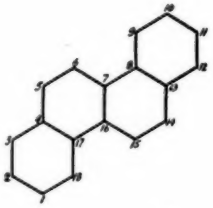
Anthracene $=4+48z+150z^2+163z^3+58z^4+6z^5,$

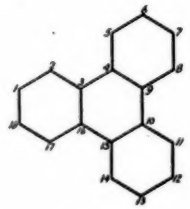
Phenanthrene  $=5+47z+148z^2+165z^3+59z^4+5z^5,$

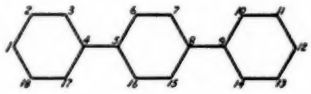
Naphthacene $=5+110z+649z^2+1556z^3+1646z^4+750z^5+138z^6+8z^7.$

1,2 Benzanthracene  $=7+112z+642z^2+1551z^3+1654z^4+754z^5+135z^6+7z^7,$

3,4 Benzophenanthrene  $=8+116z+636z^2+1542z^3+1663z^4+760z^5+131z^6+6z^7,$

Chrysene  $=8+117z+634z^2+1541z^3+1667z^4+759z^5+129z^6+7z^7,$

Triphenylene  $=9+117z+645z^2+1557z^3+1659z^4+744z^5+125z^6+6z^7,$

Terphenyl  $=8+81z+384z^2+1000z^3+1528z^4+1279z^5+503z^6+76z^7+3z^8.$

In the resolution of several of the above figures, it is convenient to make use of a further rule which can easily be derived from the one above: Let $D_{p,\ q}$ be the polynomial corresponding to two straight chains, of p and q orbitals, respectively, which are not connected to each other. Then

$$D_{p,\ q}=C_{(p+q)/2}+(z-1)D_{p-1,\ q-1}$$

$$=\sum_{k=0}^{(p+q-|p-q|)/2}(z-1)^k C_{(p+q)/2-k}.$$

Thus

$D_{7,5}=$ $=C_6+(z-1)C_5+(z-1)^2C_4+(z-1)^3C_3+(z-1)^4C_2+(z-1)^5C_1,$

$=12z+32z^2+62z^3+20z^4+6z^5.$

IV. The Molecule Contains an Unpaired Electron

This type of problem arises in the treatment of free radicals. The procedure is simply to introduce a "phantom orbital" X, containing a "phantom electron," which is formally bonded to the unpaired electron of the molecule.[1] The exchange integrals between this phantom orbital and the real orbitals are set equal to zero. As before, it is desirable first to obtain expressions for straight chains, and we find at once that the polynomial F_N, corresponding to the chain of $2N-1$ orbitals, is given by the expression

$$F_N=(1/z)D_{2N-1,\,1}=(1/z)[C_N+(z-1)C_{N-1}].$$

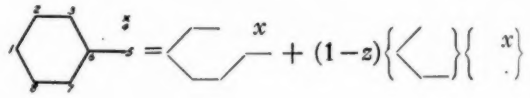
(The factor $1/z$ occurs since the bond to the phantom orbital X, although ineffective, is not considered to increase the degree of excitation.)

The first few members of the series are:

$$F_1=1,$$
$$F_2=2,$$
$$F_3=3+2z,$$
$$F_4=4+8z+2z^2,$$
$$F_5=5+20z+15z^2+2z^3.$$

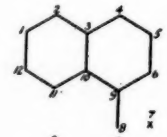
It is interesting to observe that the coefficients k_i appearing in F_N are the same as those appearing in R_N, but that their order is reversed.

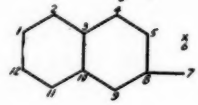
In the treatment of molecules containing rings, the same procedure can be used as before. For the phenylmethyl radical, for example, we have

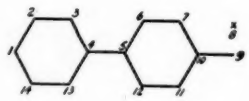


$=F_4+(1-z)C_2F_1=5+8z+z^2.$

A few other results are given below:

α-naphthylmethyl  $=10+46z+58z^2+18z^3,$

β-naphthylmethyl  $=9+50z+54z^2+18z^3+z^4,$

Biphenylmethyl  $=13+66z+148z^2+147z^3+51z^4+4z^5.$

Application to the Calculation of Molecular Energies

The author has shown recently[6] that for a hydrocarbon molecule which does not contain any odd membered rings the energy which results from the simplified Heitler-London procedure of Pauling and his co-workers[1] can be expressed as

$$W=Q+\frac{\sum_R a_R g_R n_R}{\sum_R a_R g_R}\alpha,$$

where g_R is the number of structures of type R which appear with the coefficient a_R in the complete eigenfunction for the molecule, and n_R is

[6] G. W. Wheland, J. Chem. Phys. **3**, 230 (1935).

the number of effective bonds in any one of the structures R. Q and α are, as usual, the Coulomb integral and the single exchange integral, respectively. If all the structures of the ith degree of excitation are assumed to have an average coefficient a_i, then the above equation becomes

$$W=Q+\frac{\sum_i a_i k_i (b-i)}{\sum_i a_i k_i}\alpha,$$

where b is equal to the number of effective bonds in the unexcited structures. (If there are no phantom orbitals, $b=N=$one-half the number of orbitals.)

If some method were available for estimating the coefficients a_i, the calculation of the energy of any molecule of the present type would be quite simple. The rule given in the previous paper,[6] that $a_i=(0.3)^i$ is fairly satisfactory for small molecules, but it leads to too small values of the energy (in absolute magnitude) when N becomes greater than 5. It also fails to allow for variations of the coefficients between molecules of the same size, but of quite different structure. A rather better, but equally empirical rule can be put forward tentatively:

$$a_i=(0.04-0.93/N+1.05B/N^2)^i,$$

where B is equal to the number of pairs of orbitals for which the corresponding exchange integral is α. Some results obtained by this method are given in Table I. It will be seen that they are really quite satisfactory. It is doubtful, however, if this procedure could be safely applied to molecules of widely different type from those considered here, since there is no assurance that the same rule for estimating coefficients would be at all satisfactory.[7] In particular, the assumption that a_i for a given molecule can be represented by the ith power of a constant quantity has little if any theoretical justification. The estimated coefficients may, therefore be very seriously in error, and the energy may come out approximately correct only in consequence of a cancelation of errors. Be this as it may, however, the method seems to be quite a satisfactory one from an empirical point of view, and can be applied with some assurance to the treatment of molecules which do not differ very greatly, either in size or in type, from those considered in Table I.

[7] One readily sees, in fact, that the rule is no longer very good for the free radicals.

TABLE I.

Compound	a_1	Energy Approx.	Energy Correct[a]
Benzene	0.43	$Q+2.61\alpha$	$Q+2.61\alpha$
Cyclooctatetrane	0.33	3.31α	3.30α
Cyclodecapentane	0.27	4.05α	4.03α
Phenylethylene	0.33	3.30α	3.31α[c]
Sym. Diphenylethylene	0.23	5.66α	5.59α[c]
Unsym. Diphenylethylene	0.23	5.67α	5.55α[c]
Biphenyl	0.26	4.93α	4.87α[c]
Terphenyl	0.20	7.36α	7.09α[c]
Naphthalene	0.32	4.08α	4.04α
Anthracene	0.25	5.59α	(5.53α)[b]
Phenanthrene	0.25	5.65α	(5.69α)[b]
Naphthacene	0.21	7.15α	
1,2 Benzanthracene	0.21	7.21α	
3,4 Benzophenanthrene	0.21	7.24α	
Chrysene	0.21	7.24α	(7.35α)[b]
Triphenylene	0.21	7.26α	
Butadiene	0.36	1.74α	1.73α
Hexatriene	0.31	2.45α	2.48α
Octatetrane	0.27	3.21α	3.22α[c]

[a] L. Pauling and J. Sherman, J. Chem. Phys. 1, 679 (1933). G. W. Wheland, J. Chem. Phys. 3, 230 (1935).

[b] These values were calculated from the observed resonance energies (L. Pauling and J. Sherman, J. Chem. Phys. 1, 606 (1933)) with $\alpha=-1.5$ e.v. In view of the really surprising agreement which has been found, in all other cases, between the theoretical and the observed resonance energies (cf. ref. 1), this seems a safe method for estimating the order of magnitude of the former.

[c] In these calculations, Pauling and Sherman used an approximate method of solving the secular equation. The procedure (for a justification of which see J. Sherman, J. Chem. Phys. 2, 488 (1934)) consisted in neglecting the second and higher excited structures and in arbitrarily equating coefficients. As a result, the coefficients of α appearing here are somewhat too low.

The Thermal Conductivity of Polyatomic Gases. Erratum

A. R. UBBELOHDE, *Department of Thermodynamics, Clarendon Laboratory, Oxford*
(J. Chem. Phys. **3**, 219 (1935))

PAGE 222, 6th line from the bottom: Should read, "a maximum addition of 0.02 to F" in lieu of "a maximum of 0.02 to F".

Molecular Arrangement and X-Ray Diffraction in Ionic Solutions. Errata

J. A. PRINS, *Natuurkundig Laboratorium der Rijks-Universiteit, Groningen, Holland*
(J. Chem. Phys. **3**, 72 (1935))

MY article on this subject having been printed without author's proof, the following inaccuracies occur:

Page 77, end second paragraph §7. *To be added:* It should be remarked that at a *larger* distance from the ions a *different* and more subtle rearrangement of the water molecules may take place. It is *this* rearrangement ("water II→water I") which has been considered by Bernal and Fowler in connection with the term "structural temperature." It will presumably be of importance in moderately diluted solutions. In our case, however, of *strong* solutions, where *every* water molecule is rather close to an ion, I think the rearrangement considered above ("water II→water III") is more important.

Page 78, paragraph headed by "If the case of a 1 : 10 LiI solution." *To be read:* class III mentioned in §6, instead of class II, mentioned in §4.

Page 79, beginning. *To be read:* class II (§5) instead of class III.

Page 80. *To be read:* 1.8λ instead of 2.8A.

Page 80. *To be read:* $(a+l+b+l)/2$ instead of $a+l+b+l$.

I use this occasion to remark that a more quantitative study of some points considered in this article will be published in *Physica* (Den Haag) in collaboration with Dr. R. Fonteyne.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Raman Spectrum of Orthophosphoric Acid

The Raman spectrum of orthophosphoric acid has been investigated by Nisi.[1] He found frequency differences of 356, 498 and 911 cm^{-1} for 84 percent (by weight?); 512 and 906 for 50 percent; and 505 and 898 for 25 percent. The writers have made a study of H_3PO_4 at concentrations ranging from 50 mole percent (the highest available) to 10 percent. The results agree with those of Nisi.

One strong line appears at all concentrations. Measurements of it are as follows (with the excitation by 4358A accurate to about 2 cm^{-1}):

Mole percent		*Excited by 4358*	*Excited by 4047*
50	22,029	909	
	23,798		907
40	22,033	905	
	23,801		904
30	22,037	901	
	23,807		898
20	22,042	896	
	23,807		898
10	22,043	895	
	23,812		893

When the product of exposure time and mole percent is made constant, this line appears to have the same intensity at all concentrations. A shift in frequency of about 14 cm^{-1} is clearly indicated.

Other lines which appear at 50 percent are: 22,448 (490), 22,579 (359), 23,607 (909), and 24,212 (493). 490 and 359 cm^{-1} are broad and weak. The 23,607 line is probably excited by 4078A. These weak lines could not be measured at lower concentrations, except 23,624 (892) at 10 percent.

MYRON A. JEPPESEN
RAYMOND M. BELL

Department of Physics,
Pennsylvania State College,
April 22, 1935.

[1] Nisi, Jap. J. Phys. **5**, 119 (1929).

The Vitreous State

In a recent article,[1] Zachariasen has commented my paper on the vitreous state, published in the January number of this Journal.[2] In the following, the comments of Zachariasen are briefly discussed.

My statement that Zachariasen's viewpoint is only adaptable to cases in which the oxygen polyhedra form three-dimensional networks, is based on the fact, that Zachariasen only treats this case. The requirement of a three-dimensional network is the fourth of his rules which he thinks must be fulfilled if an oxide is to form a glass. Later, this rule is also generally applied to oxides, without considering the possibility that the corresponding crystal structure could be characterized by a network of oxygen polyhedra, extended in less than three dimensions. Also in his summary, Zachariasen speaks only of three-dimensional networks.

Zachariasen further says that it is "no real progress to present a theory for the structure of glass in terms of the equally unknown structure of the liquids." I think, in contrary, that this is the most logical way of attacking the glass problem. We know from several analogies that the liquid and vitreous states must be closely connected and we then make use of conceptions of the liquid state which are so general and obvious that they are very likely to be true. I do not think this is more dangerous than direct comparisons between the vitreous and the crystalline state.

The fact that I have not given any detailed description of the structure of the fragments, possible in a glass, is caused by the multitude of structures existing in different glasses and by the variation which can be expected for the different fragments in one definite glass. I have pointed out the importance of definite coordinations within the fragments and I think a consideration of this fact is sufficient for making clear the general structure of a fragment.

It is a matter of course, that a glass, built according to my theory, must be optically clear as the constituting fragments or groups are small compared to the wavelength of light.

It is my opinion that it is the tendency of certain atoms to attain a certain oxygen coordination and the strength with which oxygen is bound to these atoms which is the main cause of the glass forming tendency of vitreous oxides. As Zachariasen remarks, I added in the summary that "the glass forming tendency . . . seems to be especially large when the corresponding crystals contain radicals or molecules unlimited in one or more dimensions" but I do not admit that this statement is too general when it is read in connection with the preceding sentence which implies that these groups must be contained in the melt and kept together with strong (probably in many cases homopolar) forces. In this way I explained why SiO_2 can form glass and

BeO not. The fact that TiO_2 is not known in the vitreous state is also explained by the more basic character of this oxide, which is connected with weaker bonds between Ti and O.

Concerning H_3PO_4, I explained its glass forming tendency by assuming larger groups than $(PO_4)^{-3}$ to exist in the melt but I did not discuss the question whether these groups are formed by polymerization of $(PO_4)^{-3}$ radicals only or if hydrogen was necessary at the construction.

I consider the glasses as supercooled liquids in which the supercooling tendency is caused by groups in the melt which can be added with difficulty directly to the lattice and within which the atoms are kept together by so strong forces as to make their separation difficult. My theory of the structure of glasses is based on this assumption and the problem of the glass forming tendency of a substance is brought back to the question whether such groups are to be expected in the melt. Zachariasen, on the contrary, has assumed a certain type of structure, characterizing the vitreous state. Starting from the corresponding crystal structures, he then discusses the possibility of constructing the vitreous structure.

GUNNAR HÄGG
Institute of General and Inorganic Chemistry,
University of Stockholm,
April 2, 1935.

[1] W. H. Zachariasen, J. Chem. Phys. **3**, 162 (1935).
[2] G. Hägg, J. Chem. Phys. **3**, 42 (1935).

The Magnetic Properties of the Phenanthroline Ferric Complexes

We have investigated the magnetic susceptibilities of the complex ions formed by the base ortho-phenanthroline with ferric ion. Blau, who discovered some forty years ago the extraordinary stability of the complex metallic ions formed by this base, reported that two ferric complexes are formed, which are not directly interconvertible. One of these is intensely blue in color; can be obtained only by oxidation of the ferrous complex; and has, as the analysis of several solid salts demonstrate, the formula $Fe(C_{12}H_8N_2)_3^{+++}$. The other is brown, and is formed by the direct reaction of ferric salts with phenanthroline. We have obtained a solid brown salt whose analysis corresponds to the formula $[Fe(C_{12}H_8N_2)_2(H_2O)(OH)]Cl_2$, but other compounds are undoubtedly also present in the solutions obtained by addition of phenanthroline to solutions of ferric salts. As is indeed to be expected of complexes as stable as these, their formation from ferric ion is accompanied by a very considerable decrease in magnetic susceptibility. According to the theories of Lewis and Pauling the linkages concerned are therefore to be considered as of the shared electron rather than of the ion-dipole type. From measurements in aqueous solution the atomic susceptibility of the iron atom in the blue complex is 2446×10^{-6} which is practically identical with the value observed with ferricyanide ion and generally accepted as the normal one for coordinatively bound ferric ion. The corresponding value for the brown complex is, however, only 826×10^{-6}. The low value for the magnetic moment, 1.4 Bohr magnetons, to which this leads is perhaps to be attributed to the existence in a single molecular grouping of two or more iron atoms so oriented that their moments partially neutralize each other. There are indeed other indications, now under investigation, that the brown complex has a higher molecular weight than would correspond to a single iron atom per molecule.

GEORGE H. WALDEN
LOUIS P. HAMMETT
ALLISON GAINES, JR.

Department of Chemistry,
Columbia University,
May 6, 1935.

The Decomposition of Hydrogen Peroxide by the Irradiation of Its Aqueous Solution with X-Rays*

Gas-free (unbuffered) solutions of hydrogen peroxide were irradiated with x-rays and the resulting decomposition determined by electrometric titration[1] and by gas analysis. None or a very small amount of hydrogen is produced, the decomposition proceeding essentially according to: $2H_2O_2 = 2H_2O + O_2$. Over the range of concentrations (0.0001 to 0.1 moles H_2O_2/1000 cc) and x-ray intensities (3 to 15 r/sec.) used, the number of moles of hydrogen peroxide decomposed per unit of dosage increases as the square root of the concentration and decreases as the square root of the x-ray intensity. (Fig. 1.) For a special set of conditions, the

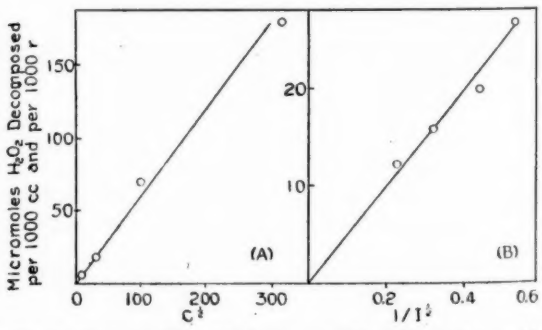


FIG. 1. Decomposition of hydrogen peroxide as a function of: (A) Square root of concentration (C in micromoles per 1000 cc) for an intensity of 9.5 r/sec. (B) Inverse square root of intensity (I in r/sec.) for a concentration of 1.0 millimole H_2O_2 per 1000 cc.

dependence of the decomposition** on the temperature was determined between 0° and 50°C. (Fig. 2.) The temperature coefficient shows a remarkable rise with the temperature; its value, between 15°C and 25°C is 1.18.†

A comparison with results[2-8] obtained for the decomposition of hydrogen peroxide with light is of interest. The evidence is not wholly clear, but the increase of the quantum efficiency with the square root of the concentra-

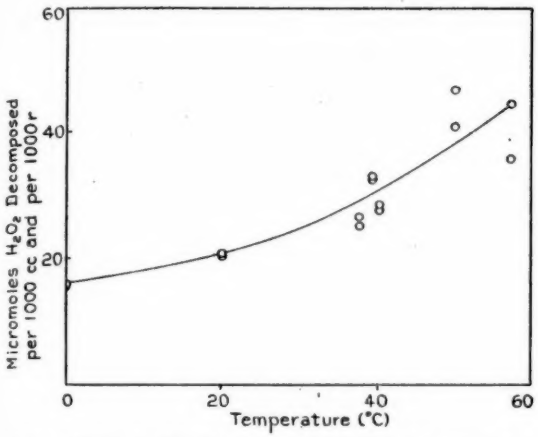


FIG. 2. Decomposition of hydrogen peroxide as a function of the temperature for an x-ray intensity of 3.0 r/sec. and a concentration of 1.0 millimole H_2O_2 per 1000 cc.

tion (except when the concentration is very large)[2, 8] and with the inverse square root of the intensity, appears consistent with the experimental data. This would be in agreement with the present results if we assume that the decomposition in the case of x-rays is not due to the direct activation of the hydrogen peroxide molecules by the x-ray electrons, but that the primary process is the activation of water molecules[1, 9–13] followed by the transfer of energy from these activated molecules to the hydrogen peroxide.†† On this assumption, the quantum efficiency (in the case of light) should be compared to the number of moles of hydrogen peroxide decomposed per unit of x-ray dosage. It should also be noted that if the decomposition were due to the direct activation of the hydrogen peroxide molecules by the x-ray electrons, in the extreme case as many as 10,000 molecules of hydrogen peroxide would be decomposed for each hydrogen peroxide molecule activated, an unlikely number in view of the relatively short chains observed in the case of light.

HUGO FRICKE
Walter B. James Laboratory for Biophysics,
The Biological Laboratory,
Cold Spring Harbor, N. Y.,
March 30, 1935.

* I am indebted to Dr. E. R. Brownscombe for assisting with these measurements.

** The decomposition of nonirradiated blanks was corrected for, and amounted, at 50°C, to a few percent of that produced during irradiation.

† For the decomposition by light, Allmand and Style, reference 2, found the temperature coefficient (at room temperature) to be: 1.42 for $\lambda = 3650$A, and 1.28 for $\lambda = 2750$A.

†† On this assumption, in our experiments the number of molecules of hydrogen peroxide activated would be expected[1, 9–13] to be of the order of 10^{13}/cc/sec. With light, intensities producing from 10^{13} to 10^{16} activations/cc/sec. have been used.

[1] Fricke, J. Chem. Phys. **2**, 556 (1934).
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The Oxidation of the Nitrite to the Nitrate Ion by the Irradiation of Its Aqueous Solutions with X-Rays

Gas-free solutions containing the nitrite ion were irradiated with x-rays and were analyzed for hydrogen and oxygen; and for nitrite by electrometric titration with potassium permanganate. The nitrite ion is oxidized to the nitrate ion and hydrogen liberated in the equivalent amount. The amount of nitrite oxidized is independent of the concentration of the nitrite ion from 0.05 to 100.0 millimoles/1000 cc and of the hydrogen ion concentration from pH = 2.0 to 11.0 and equals 0.55 micromole/1000 r/1000 cc. It is concluded that the transformation is due to water molecules activated by the x-rays, according to:

$$NO_2^- + (H_2O)_{act} = NO_3^- + H_2.$$

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The Far Ultraviolet Absorption Spectra and Ionization Potentials of the Ethyl Halides

The absorption spectrum of ethyl iodide is essentially similar to that of methyl iodide[1] and starts at about the same wavelength. Two electronic series containing a large number of terms appear. The upper members can be extrapolated in the form of Rydberg series to ionization potentials of 9.295 ± 0.005 and 9.885 ± 0.005 volts. Thus a difference of about 0.6 volt is maintained in going from methyl to ethyl iodide though the ionization potentials of the latter are diminished by 0.2 volt relative to the corresponding ones in methyl iodide.

The first resonance bands of ethyl bromide start around 1770A and thus suffer a short wavelength shift of 15A relative to the corresponding bands in methyl bromide. They are much more diffuse but two series limits can still be observed. These can be extrapolated to the ionization potentials 10.24 ± 0.01 and 10.56 ± 0.01 volts corresponding to a diminution of 0.25 volt relative to the values obtained for methyl bromide.[2] Part of the difficulty of observing these limits is a background of continuous absorption arising from excitation in the CC bond.

In the case of ethyl chloride only the first few bands are sharp. These are shifted to long wavelengths by about 0.36 volt relative to the analogous bands in methyl chloride. The electronic difference of 0.08 volt is maintained and it is estimated that the ionization potentials of ethyl chloride are about 0.38 volt less than those given for methyl chloride.

The above data provide considerable support for the suggestion put forward by the author[3] that the dipoles of methyl and ethyl groups have a strong influence in reducing the ionization potentials of electrons in adjacent bonds. R. S. Mulliken[4] has shown that the spectra of the

alkyl halides are due to the excitation of nonbonding $np\pi$ electrons from the halogen atom. It is here assumed that the additional strength of the C_2H_5 dipole over the CH_3 dipole is responsible for the diminution of the ionization potentials of the ethyl relative to the methyl halides. The increasing effect as we go from the iodide to the chloride is explained by the decreasing combination radii of the halogen atoms. This brings the dipole closer to the electron considered and thus increases its effect.

This dipole hypothesis has also been useful in explaining the deviations of the first few electronic states from Rydberg formulas which occur if the spectrum starts at fairly long wavelength (i.e., around 2000A). These deviations are negligible in the case of C_2H_2, H_2S and CH_3Cl which start around 1500–1600A. In these cases the radii of the orbits of the first excited states are so large that the effect of the dipole disappears after the first jump. In methyl and ethyl iodide the first and second excited states are still strongly affected by the dipole. The hypothesis can also be applied to give a satisfactory explanation of the magnitudes of the long wavelength shifts of the first resonance bands of the ethyl halides which appear to be a little anomolous at first sight.

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